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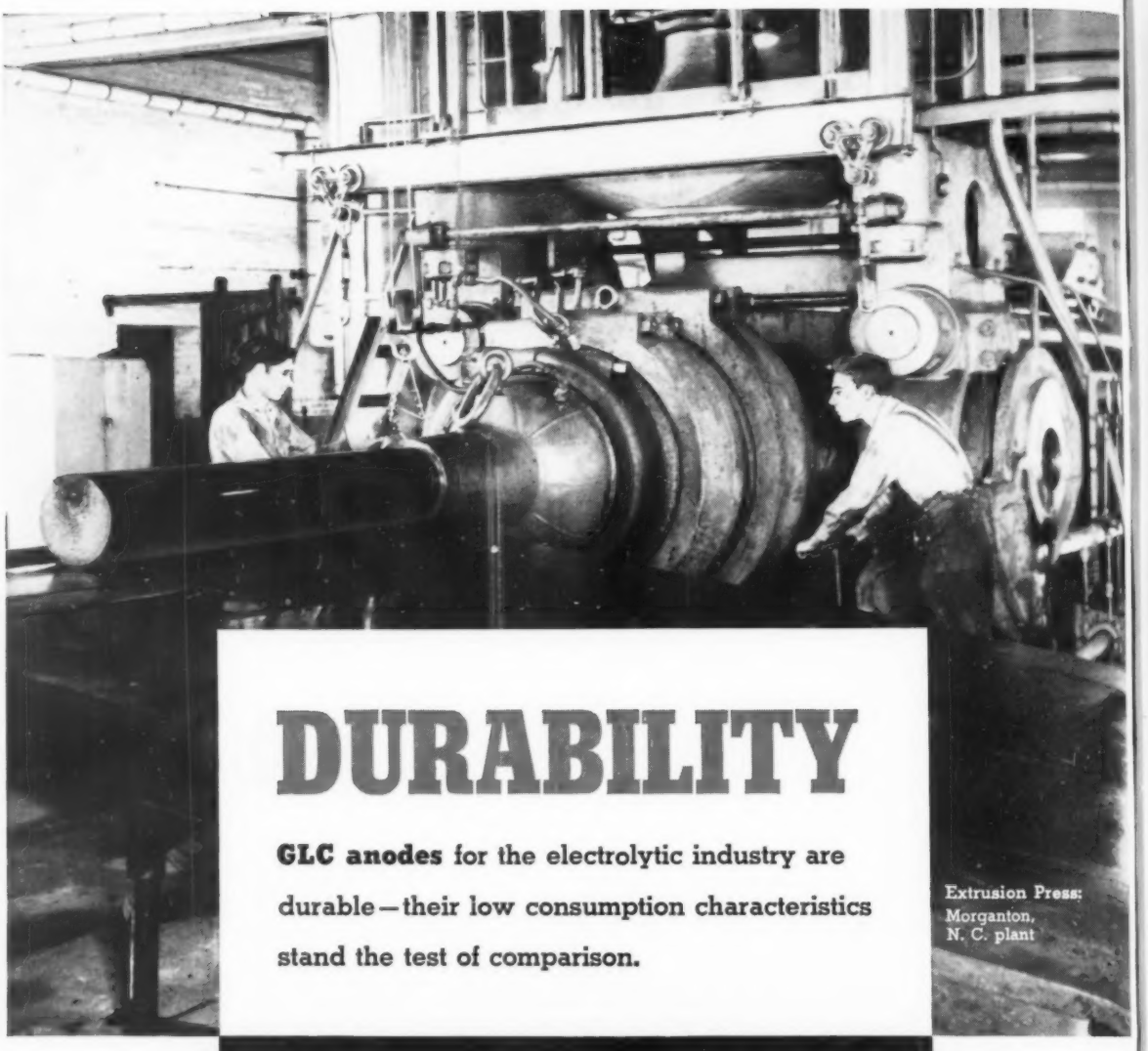

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OCTOBER, 1951 VOLUME 98 • NUMBER 10

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The Effect of Impurities in Nickel Solutions

...and Methods of Purification

Bright nickel baths are usually much more sensitive to impurities than are matte nickel solutions, and certain contaminants are much more harmful than others. The effect of these contaminants and some methods of purification in current use are indicated below.

ARSENIC tends to lower the tensile strength of nickel deposits. It also causes dull, streaked, brittle deposits. The Liscomb method successfully removes arsenic.

CALCIUM sulphate in a nickel bath causes roughness, pitting and dullness. Filtration readily removes suspended crystals.

CHROMIUM contamination tends, generally, to reduce cathode efficiency and produce deposits in a marked degree of stress. The contaminant can be removed by the Liscomb method, by precipitation at a high pH, or by formation of insoluble lead chromate.

COPPER has the effect of producing dull, dark deposits in the low current density regions, and general fogging of the deposit in other regions. Most effective removal of traces is achieved by a low current density electrolysis at low pH, high temperature and high rate of agitation.

IRON as colloidal ferric hydroxide causes roughness. In a soluble form it codeposits with nickel. This impurity causes one form of pitting. Low current density electrolysis or high pH treatment removes iron.

LEAD causes dark, streaked deposits, and non-adhesion of nickel. Low current density electrolysis removes lead.

NITRATES in a nickel solution strongly depress current efficiency. High concentrations may stop deposition entirely. Electrolytic reduction at the cathode removes this impurity.

ORGANIC SUBSTANCES of many types, including grease, waxes, dust, etc., are detrimental. Their removal usually involves oxidation or carbon filtration, or both treatments.

SULPHUR, in the form of organic compounds, has a brightening effect in many types of nickel solutions. Nickel sulfide is harmful because it results in evolution of hydrogen sulfide and precipitation of sulfides. Although carbon treatment removes some organic compounds containing sulfur, and a high pH precipitates sulfides, there is no general method for removing traces of sulfur compounds.

ZINC in amounts of 0.007 oz/gal is a brightener in dull-nickel plating baths, but higher concentrations yield brittle deposits which may be dark or streaked. The Liscomb method can reduce zinc concentrations. However, low current density electrolysis is the most widely accepted process.

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Editorial

Detroit at 250

GREETINGS TO DETROIT on her 250th anniversary! Coming to the Nation's fifth city, the Society will hold its 100th meeting under appropriate circumstances. Established in 1701 by Cadillac as a frontier village of a hundred settlers, Detroit became the oldest city west of the Atlantic seaboard. For the first 200 years, the quiet life of this community was interrupted only by the American Revolutionary War, occasional Indian raids and the westward advance of the railroad. It was with the turn of the century and the establishment of the automotive industry that Detroit became what she is today, the symbol of American industrial development and mass production. Thus, within the lifetime of The Electrochemical Society, Detroit has grown tenfold in population and justified her position as the world's automobile center. The income per capita of her people is said to exceed that of any other city. Enterprise and ingenuity have been her noteworthy characteristics.

Electrochemical industry has made large contributions to the automobile. Abrasives, alloy steels, light metals, and many other products of the electric furnace and the electrolytic cell have been essential raw materials. The automobile industry has long been the largest user of electroplated finishes and of storage batteries. Indeed it is not too much to say that this industry has given the principal impetus to modern developments in both electroplating and storage cells. Thus, it is fitting that electrochemists should join Detroit in her anniversary celebration. Next spring in Philadelphia, The Electrochemical Society will celebrate its semicentennial and at that time provide a further occasion to review the electrochemical developments of the past half century which have contributed so much to American life. —RMB

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—FROM REVIEWS

A Romance in Research

The LIFE *of* CHARLES F. BURGESS

Student — Teacher — Researcher — Industrialist

By Alexander McQueen

With a foreword by George W. Heise

and a technical appendix by O. W. Storey

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* Dr. Burgess was a Charter Member of the Society.

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Vapor Deposition of Metals on Ceramic Particles[1]

JAMES E. CLINE AND JOHN WULFF

Massachusetts Institute of Technology, Cambridge, Massachusetts

ABSTRACT

The coating of ceramic particles with metal by vapor deposition was investigated for the production of high-temperature metal-ceramic bodies. Methods are described for coating particles of ceramics such as silica, silicon carbide, and alumina with molybdenum deposited by hydrogen reduction of molybdenum pentachloride and with nickel deposited by decomposition of nickel carbonyl. The particles must be kept in motion by gas flow or by mechanical agitation during the coating process. In the presence of titanium carbide the decomposition of nickel carbonyl proceeds abnormally, leading to the formation of carbon.

INTRODUCTION

In the development of metal-ceramic bodies for high-temperature use it was considered that a uniform distribution of the metal phase around each ceramic grain before sintering might lead to improved physical properties of the metal-ceramic body. Increased thermal conductivity, due to a continuous metallic network and improved strength, was among the possible advantages. This investigation was concerned with the application of the vapor deposition of metals from their volatile compounds in order to form a thin continuous coating of metal around each ceramic grain.

The vapor deposition of various metals has been studied both in this laboratory (1) and in others (2–4). The metals chosen for this study, molybdenum, iron, and nickel, were those for which the technique of vapor deposition had been developed and which were of interest in the fabrication of metal-ceramic bodies. The ceramic materials investigated were silica sand, silicon carbide, alumina, and titanium carbide. It is believed that the vapor coating technique could be applied to many other combinations of metals and ceramics, but as shown in this work, there are limitations placed both on the choice of metal and on the choice of ceramic.

VAPOR DEPOSITION OF MOLYBDENUM

The apparatus used for coating ceramic particles with molybdenum is shown in Fig. 1. The mixture of molybdenum pentachloride vapor and hydrogen was produced by passing hydrogen over molybdenum pentachloride heated in the evaporator at a temperature of 200°C. Solid pentachloride was stored in a capsule fused to the evaporator and the pentachloride could be added to the evaporator as needed by melting a portion with a torch. A heated sleeve at 210°C was used to prevent condensation of the pentachloride before reaching the reaction zone.

In order to obtain a uniform deposit of molybdenum on the ceramic grains, it is essential that they be in constant movement. Otherwise the deposited metal will cause all or part of the charge to be sintered together. In the apparatus illustrated, the flow of the gas, 47 liters of hydrogen per hour, was sufficient to fluidize the charge and keep the particles in motion. Since the problem of fluidization of solid particles in a gas stream is of great importance in the cracking of petroleum, a great deal of work (5–7) has been published in the field.

The separation of solid particles from the gas stream was partially accomplished in the small-scale apparatus used in this investigation by enlarging the cross section from 10 to 20 mm, thereby decreasing the linear velocity of the gas stream. A more effective method would be the use of cyclone separators or filters.

No difficulty was experienced in coating relatively coarse silica sand grains of mesh sizes −48 +65, −150 +200, or −200 +325 at a plating temperature of 650°C. In Fig. 2, a cross section of several grains of mesh size −48 +65 is shown coated with molybdenum. The coated grains had a bright metallic appearance.

A sample of silica sand grains of −200 +325 mesh size, coated with about 20 per cent by weight of molybdenum, was hot-pressed at 1600°C. At this temperature the silica grains were plastically deformed and a compact was formed with a molybdenum network, as shown in Fig. 3.

For the production of metal-ceramic bodies, it is desirable in most cases to use finer grains. Attempts to coat grains of −325 mesh were not so successful in the small-scale apparatus. One difficulty is the relatively great size distribution of the particles in the −325 mesh size which makes it difficult to have enough gas flow to fluidize the mass of particles

[1] Manuscript received April 16, 1951. This paper prepared for delivery before the Washington Meeting, April 8 to 12, 1951.

without blowing a large portion of the particles out of the coating zone. For efficient operation of the vapor deposition method of coating, it is evident that a fairly narrow distribution of particle sizes must be used if fluidization by the gas flow is employed for agitation.

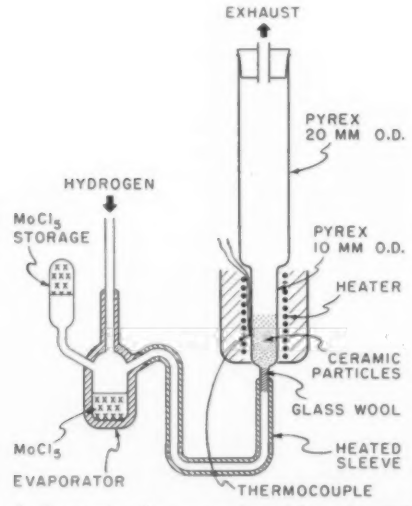

FIG. 1. Apparatus for vapor deposition of molybdenum on ceramic particles.

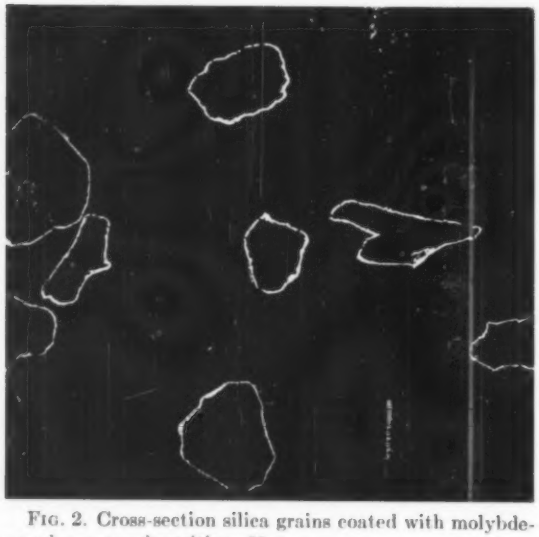

FIG. 2. Cross-section silica grains coated with molybdenum by vapor deposition. 50×.

In order to avoid the necessity of careful sizing of particles, attempts were made to use mechanical methods of agitating the grains during the coating process. A mechanical stirrer did not operate well because molybdenum deposited upon the stirrer and also a poor distribution of molybdenum on the grains was obtained.

Several methods of agitating the mass of grains by shaking the plating chamber were tried. Silicon carbide and alumina of −325 mesh were coated with molybdenum but the efficiency was low, mechanical difficulties were not satisfactorily overcome, and poor distribution of the deposit was obtained. It is believed that fluidization of the ceramic grains by gas flow offers the best opportunities for future development of the coating process. Coating of titanium carbide grains with molybdenum from the pentachloride was not successful due to the reaction between the carbide and the pentachloride to form volatile titanium tetrachloride at the plating temperature of 650°C.

Vapor Deposition of Iron

By methods similar to deposition of molybdenum from molybdenum pentachloride and hydrogen, iron

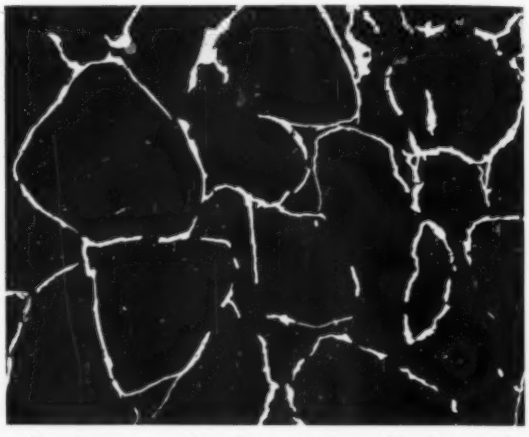

FIG. 3. Cross section of compact formed by hot-pressing of molybdenum-coated silica grains. 250×.

was deposited by hydrogen reduction of ferric chloride vapor. However, an additional difficulty was encountered. At the plating temperature of 650°C the tendency of iron to sinter was so much greater than that of molybdenum that no successful coatings of iron were obtained.

This tendency to sinter at the plating temperature is thus a fundamental disadvantage of the vapor deposition process. Coating of ceramic grains with refractory metals, such as molybdenum, tungsten, or tantalum, is probably feasible at a temperature in the neighborhood of 650°C. One can then consider the hydrogen reduction of the volatile chlorides as applicable to this class of metals. For more easily sintered metals as iron or nickel, it is thus necessary to reduce the coating temperature. The decomposition of volatile carbonyls, occurring at much lower temperatures, was thus considered to be preferable for the lower-melting metals.

Vapor Deposition of Nickel

Due to the extremely poisonous properties of nickel carbonyl, it was considered advisable not to attempt to store the carbonyl, but to prepare fresh quantities for each experiment. Nickel formate was reduced to nickel by heating at 190°C in the presence of hydrogen. Then nickel carbonyl was prepared by passing carbon monoxide over the nickel at 50°C. The carbonyl was condensed in a trap cooled by solid carbon dioxide.

The plating chamber used for deposition of nickel from the carbonyl was similar to that shown for molybdenum plating in Fig. 1. The plating temperature was, however, only 235°C. The ceramic grains were fluidized by a stream of hydrogen carrying the carbonyl vapor. In this way, grains of silica, alumina, and silicon carbide were coated with nickel.

When an attempt was made, however, to coat titanium carbide with nickel, an unexpected effect was encountered. In addition to the usual decomposition of the carbonyl to form metallic nickel and carbon monoxide, carbon appeared in the large tube above the plating zone and in the plating zone itself. This effect was observed only in the presence of titanium carbide and it is not known whether any other materials will cause this reaction. It is possible that the carbide is an active agent in the nucleation of graphite, and thus would catalyze the decomposition of freshly formed carbon monoxide to carbon and carbon dioxide. In this connection, it is of interest to report that carbon did not form when carbon monoxide was passed over titanium carbide in the absence of nickel carbonyl. Further investigation of the mechanism of the carbon formation may be of interest with possible applications to the nucleation of graphite in the iron-carbon system.

Acknowledgment

The authors wish to express their appreciation to the Air Materiel Command for financial support of this investigation, and to W. M. Kisner and R. T. Thurston for their assistance in the experimental work.

Any discussion of this paper will appear in a Discussion Section, to be published in the June 1952 issue of the Journal.

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Thermogalvanic Potentials

I. The Application of Thermodynamics to Thermogalvanic Data[1]

(A Study of the Silver Chloride Electrode from 25° to 90°C)

HARRY LEVIN[2] AND CHARLES F. BONILLA[3]

The Johns Hopkins University, Baltimore, Maryland

ABSTRACT

Thermogalvanic data may find application in the approximate determination of thermodynamic constants, in the measurement of concentration changes in industrial processes, and in the interpretation of thermal corrosion.

Ag/AgCl thermogalvanic cell data were obtained at cell temperature differences ranging from 0° to 65° C. It was found that the electrolyte species and concentration influence the value of standard emf calculated from the measured potentials.

INTRODUCTION

A thermogalvanic cell consists of two similar electrodes maintained at different temperatures and connected by a bridge of electrolyte.

The processes that constitute a thermogalvanic cell, particularly the electrical energy and entropy exchange processes, are of special interest to thermodynamicists in that they involve the application of thermodynamic concepts where over-all temperature equilibrium is not established. Corrosion engineers, too, must recognize this phenomenon, for yearly it takes a toll of industrial equipment (1).

Reversible thermogalvanic electrodes properly calibrated are applicable to the rapid recording of varying concentration in continuous processes at elevated temperature, such as in the production of synthetic phenol from benzene halides. In such systems at high pressures, the electrolyte connecting tube or bridge can be led through a pipe to the cold electrode.

The thermogalvanic cell appeared to be a promising avenue of research in the 1890's; and, accordingly, much experimentation was carried out at that time (3, 5, 8, 16). Unfortunately, theories of electrolytic solutions and electromotive forces were not advanced sufficiently to give direction and profit to this research. Since then, the subject has been considered only infrequently (2, 7, 19).

The fact that the electromotive force of the thermogalvanic cell is attributable to a temperature difference accounts largely for the lack of research, for it was recognized that the cell is not in thermal equilibrium, and it was suspected that irreversible processes influenced the electrode potentials (4).

On the other hand, Buffington (2) stated that nonthermodynamic factors may not influence the thermogalvanic cell potential, and, if this is so, standard thermodynamic relations for reversible processes apply despite temperature differences. In brief, apart from conditions of strain, he claimed that a reversible electrode is influenced only by the temperature, the pressure, the concentration and species of the particular solutes, and the species of the solvent in its immediate vicinity. Buffington further contended that, on the basis of the above reasoning, the Nernst equation, $E = E^0 \mp \frac{RT}{\eta \mathbf{F}} \ln a^{\pm}$, may be used to determine the half-cell potential of each electrode.

If Buffington's hypothesis is correct, a thermogalvanic cell using reversible electrodes is applicable to the determination of standard emf's, entropies of single ion species, and dissociation constants. This paper examines the above view by measuring the potential developed by the cell, Ag/AgCl/mMCl/AgCl/Ag, where one half cell is maintained at constant temperature T_R and the other half-cell temperature is adjusted to various values T_H. MCl is a chloride electrolyte.

Three chloride electrolytes were used, and the concentration of each was varied. Thermodynamic relations involving standard electromotive force and entropy were then applied to the measurements obtained.

EXPERIMENTAL METHODS AND DATA

Apparatus

The apparatus used in this research differed from other thermogalvanic cells in that the electrolyte

[1] Manuscript received October 20, 1950. This paper, prepared for delivery before the Washington Meeting, April 8 to 12, 1951, is a condensation of Mr. Levin's Dr. Eng. Dissertation in Chemical Engineering, available for further details through the Johns Hopkins University Library.

[2] Present address: Ronald Research Laboratories, Inc., Baltimore, Maryland.

[3] Present address: Columbia University, New York City.

connecting tube was not led up and out of the constant temperature baths, but instead passed horizontally through apertures in the walls of the baths (Fig. 1). This arrangement had many practical advantages, principally resulting from the absence of a hydrostatic head at the tops of the half cells, permitting electrodes and thermometers to be readily inserted and removed. Also thermal diffusion and complicating Soret effects are negligible in a cell of this type, since convection currents are appreciable.

The apparatus consisted of the cell and the two constant temperature baths equipped with heaters, stirrers, and thermal regulators. The apparatus and all electrical instruments were grounded to a common sheet metal base to avoid stray currents. An L & N #7673 thermionic amplifier, a potentiometer, and an external galvanometer measured the emf to an accuracy of 0.02 mv. The thermionic amplifier was employed because the resistance of the long, small-diameter connecting tube was high. Also, it was effective in minimizing current drain and polarization during balancing. Silver wires connected the amplifier to the electrodes in order to avoid thermocouple emf corrections.

Preparation of Electrodes and Electrolytes

The silver-silver chloride electrodes were of the thermal electroplated type, prepared according to the directions of Smith and Taylor (17). They were equilibrated (17) for at least two days prior to use. For the measurements of cell potential, only electrodes with initial differences in emf at room temperature of less than 0.02 mv were employed.

The electrolytes employed were aqueous KCl, HCl, and CsCl. The KCl was obtained from the National Bureau of Standards. It had been prepared according to the directions of Pinching and Bates (14), and contained less than 0.002 per cent of interfering Br^-. Twenty per cent HCl was obtained by distilling constant boiling HCl solution and collecting the middle third. C. P. CsCl was obtained from the Amend Drug and Chemical Company. It was not further purified.

The cell and the CsCl and HCl electrolytes were thoroughly deoxygenated by evacuation and bubbling with purified nitrogen. It was observed that the measured potential of the CsCl neutral salt cell was independent of O_2, but the HCl cell emf appreciably increased upon deoxygenation (18), as shown by the two lowest curves in Fig. 2.

Emf Measurements

In taking data, up to 2 days was allowed between points to insure that no slow aging process was affecting the reading. In general, equilibrium was established within 1 or 2 hr. Every point presented in Table I is the average of 4 cross-readings between the two electrodes at T_R (25.00°C) and the two at T_H. The colder electrodes were always positive.

The data are plotted in Fig. 2. The reversibility of the Ag/AgCl electrode is attested by the reproducibility of the emf values, and by the agreement

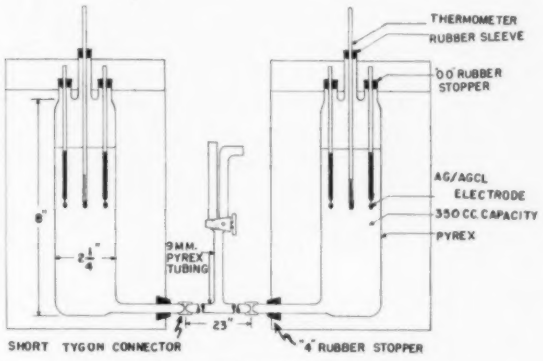

FIG. 1. Thermogalvanic cell

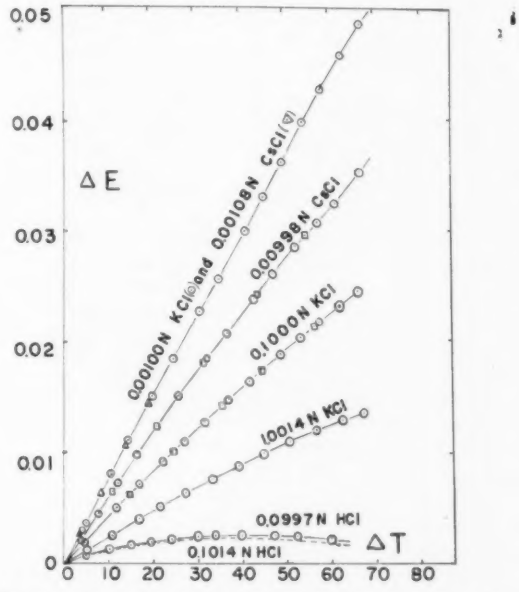

FIG. 2. Observed voltage, ΔE, for the Ag-AgCl thermogalvanic cell vs. temperature differential, ΔT, in °C. Reference electrode at 25°C. ⊡ = Descending temperature points; — — — = not deoxygenated.

between data going up and down the temperature scale for CsCl and KCl electrolytes. It is interesting to note that the points for 0.00100*N* KCl and 0.00108*N* CsCl lie on the same curve.

The Thomson Effect

Because the thermogalvanic cell and the thermocouple bear a resemblance, the unsymmetrical temperature hump test suggests itself as a method of

determining whether irreversible processes, such as the absorption and evolution of heat in the bridge of the electrolyte connecting the half cell, influence the cell potential. Buffington (2) found experimentally for the copper sulfate cell that any effects resulting from temperature differentials when heat is introduced locally in the bridge of electrolyte cancel out, the potential of the thermogalvanic cell being unaffected so long as the temperatures at the electrodes remain unchanged.

In the present experiments with the Ag/AgCl thermogalvanic cell, a flame was applied to various points along the connecting tube while the open circuit potential was measured. It was again found that the net Thomson, or temperature gradient, contribution does not vary with the temperature distribution along the connecting tube and is not linked with irreversible heat processes. In brief, the open circuit potential of a thermogalvanic cell is reversible and is determined solely by the temperature existing at the two half cells, apart from any thermocouple corrections due to the leads.

TABLE I. *Thermogalvanic data for* Ag/AgCl *electrodes,* $T_R = 25.00°C$; $\Delta T = T_H - T_R$; E = measured emf

0.00100N KCl		0.1000N KCl		1.0014N KCl		0.0997N HCl		0.00108N CsCl		0.00998N CsCl	
ΔT°C	E mv	ΔT°C	E mv	ΔT°C	E mv	ΔT°C	E mv	ΔT°C	E mv	ΔT°C	E mv
Ascending temperature (T_H increasing)											
4.00	2.99	4.61	2.03	5.14	1.31	4.71	0.73	3.80	2.88	3.65	2.20
10.57	8.15	11.87	5.09	11.25	2.82	10.59	1.29	8.31	6.35	7.86	4.70
14.35	11.03	16.87	7.18	16.68	4.09	14.77	1.63	14.08	10.87	12.25	7.39
19.83	15.22	22.27	9.28	21.22	5.10	19.35	1.95	18.92	14.72	16.55	9.89
24.60	18.46	27.08	11.16	27.30	6.40	24.02	2.18			21.27	12.52
30.41	22.84	31.62	12.88	33.29	7.65	29.85	2.40			25.87	15.07
34.76	25.83	37.25	14.95	39.32	8.88	33.83	2.53			32.38	18.57
40.53	30.15	42.03	16.70	44.96	9.98	40.85	2.63			36.80	20.88
44.76	33.34	48.71	19.06	50.86	11.07	47.22	2.69			42.76	24.08
48.84	36.47	53.27	20.59	56.73	12.12	55.01	2.49			46.95	26.23
53.37	40.11	57.67	21.98	62.57	13.00	59.40	2.30			52.38	28.77
57.80	43.10	62.05	23.45	67.00	13.65					57.15	30.82
62.50	46.07	65.90	24.66							61.13	32.68
66.86	48.79									66.70	35.29
Descending temperature (T_H decreasing)											
4.81	3.59	56 05	21.46							54.18	29.67
		44.55	17.51							43.29	24.40
		35.50	14.25							31.66	18.48
										20.92	12.47
										10.84	6.69

The Soret Effect

It is observed experimentally that when a temperature gradient is maintained in a stationary body of electrolyte, an originally uniform solution may develop a concentration gradient, such that with a polar solvent the concentration of solute at the cold end is higher. This is known as the Soret effect. To produce this effect to an appreciable extent, diffusion conditions must be optimum, and conversely, convection must be largely eliminated. This tendency for mass transfer under a thermal gradient results in an emf which becomes zero when mass transfer equilibrium is established. Accordingly (and contrary to Buffington), an emf correction appears indicated if the Soret equilibrium has not been effected. For this reason, it may be necessary to ascertain to what extent concentration gradients are present in the thermogalvanic cell under consideration.

The Ag/AgCl cell employed, due to its geometry, was not conducive to the Soret effect. However, tests were run to determine if perceptible concentration gradients did develop. Electrolyte was removed from each half cell of the 0.1N KCl and the 0.1N HCl cells after 24 and 19 hr, respectively, at 25°C temperature differences. The removed samples were allowed to reach the same temperature and then titrated. No differences in concentration were detected either in the KCl or the HCl half-cell samples, with a sensitivity of approximately 0.1 per cent.

Discussion of Results

Simple Nernst Theory Approach

The data in Table I will first be treated as if each half cell completely follows the Nernst equation

(according to Buffington's hypothesis) and as if effects due to cation, solvent, and ion diffusion influences are absent. The calculated results will be discussed as to their validity and as to whether corrections for other effects must be considered.

For the thermogalvanic cell $(Ag/AgCl)_{T_R}/mMCl/(AgCl/Ag)_{T_H}$, $Ag + Cl^- \rightleftarrows AgCl + e$ being the half-cell reaction:

$$E_R = E_R^{0\prime} + \frac{RT_R}{\mathbf{F}} \ln a_{Cl_R^-} \qquad (I)$$

and

$$E_H = E_H^{0\prime} + \frac{RT_H}{\mathbf{F}} \ln a_{Cl_H^-} \qquad (II)$$

where $E_R^{0\prime}$ is defined as the electrode emf referred to E^0 (or E_R^0) for $H_2 \rightleftarrows 2H^+ + 2e$, taken equal to zero at 25°C. Thus $E_R^{0\prime} = E_R^0$ for the electrode at 25°C, but at T_H, $E_H^{0\prime} \neq E_H^0$, where E_H^0 is the standard electrode potential at temperature H referred to the standard hydrogen electrode being equal to zero at temperature H.

Subtracting (II) from (I)

$$E \text{ meas.} = E_R - E_H$$
$$= E_R^0 - E_H^{0\prime} + \frac{R}{\mathbf{F}} (T_R \ln a_{Cl_R^-} - T_H \ln a_{Cl_H^-}). \qquad (III)$$

If equation (III) describes the thermodynamic process in its entirety, then $E_H^{0\prime}$ is independent of concentration and cation species, and Buffington's hypothesis is correct.

Mean Activity Coefficients

In calculating E_H^0 from 25° to 90°C it is necessary to know the mean activity coefficients, γ, of the aqueous solutes. Latimer's values at 25°C (10) are used. Activity coefficients at other temperatures are closely estimated by applying to successive temperature increments the value of $\frac{\partial \ln \gamma}{\partial \ln T}$ from the following relationship for dilute solutions:

$$\frac{T \partial \ln \gamma}{\partial T} = \frac{\partial \log \gamma}{\partial \log T}$$
$$= \ln \gamma \left(1 + \frac{1}{2(1 + \kappa\alpha)}\right)\left(1 + \frac{\partial \log D}{\partial \log T}\right) \qquad (IV)$$

where α is the effective ionic diameter, D is the dielectric constant, $\kappa = \sqrt{\frac{8A^2\epsilon^2 S}{1000DRT}}$, S is the ionic strength, A is Avogadro's number, and ϵ is the electron charge, $4.803 \cdot 10^{-10}$ electrostatic units. Pauling's value of α (13) and Wyman's values of D as a function of temperature (20) are used. The calculated values of γ are shown in Fig. 3.

$E_H^{0\prime}$ Values for $Ag + Cl^- \rightleftarrows AgCl + e$

After calculating the mean activity coefficients, the $E_H^{0\prime}$ values, based on the measured emf's of Table I, were obtained by equation (III) at 5° intervals from 25° to 90°C for the various concentrations and species of electrolytes, and are given in Table II. The values are uncorrected for thermal diffusion effects. The E_R^0 value at 25°C, 0.22239 v, is that of Harned and Ehlers (9).

The agreement among the values for KCl seems good, considering the wide range of concentration. The largest deviation is at T_H = 65°C and amounts to 0.94 mv. The CsCl values also agree well among themselves. The discrepancy between the two salts increases with temperature to just under 1 mv at 90°C.

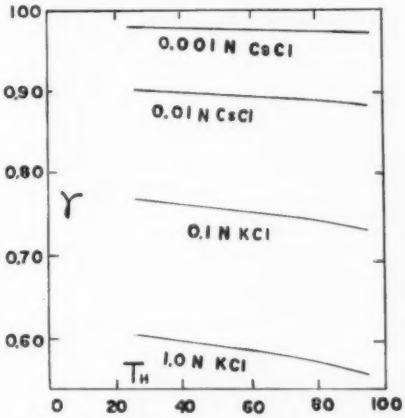

FIG. 3. Mean activity coefficients, γ, calculated from Latimer (10), vs. electrolyte temperature, T_H, in °C.

Table II appears to indicate that the Nernst equation is at least approximately correct with KCl and CsCl electrolytes. Some deviations do exist due to cation species and concentration, however, and the agreement among the $E_H^{0\prime}$ values is not sufficient to definitely establish the validity of equation (III).

Applying equation (III) to the measured data of the cell $Ag/AgCl/0.1N$ HCl/AgCl/Ag, where T_H = 30°C and T_R = 25°C, $E_H^{0\prime}$ = 0.22224 v, which disagrees completely with the $E^{0\prime}$ values for the KCl and CsCl electrolytes at the same ΔT. The abnormal behavior of H^+ (and of OH^- as well) is also reported by Tyrrell and Hollis (19) and is probably due to the high mobilities of these ion species.

Buffington noted the discrepancy when hydrogen ion electrolytes are used and called it "disturbing." More probably it demonstrates the incompleteness of his hypothesis that thermodynamic relations for reversible processes apply to the electrode reaction so long as the actual concentration is unchanged in the vicinity of the electrode.

$S^{0\prime}_{Cl^-}$ Values

Plots were prepared of $E^{0\prime}_H$ vs. T_H for the 0.1N and 0.001N KCl electrolytes and the slope of each curve read at 5°C intervals. These slopes when multiplied by $\eta\mathbf{F}$ give ΔS^0, the standard entropy of reaction for $Ag + Cl^- \rightleftarrows AgCl + e$ for the corresponding temperature and electrolyte. The absolute entropy of the chloride ion can then be computed from available absolute entropies of Ag and AgCl, since $S^{0\prime}_{Cl^-} = S^0_{AgCl} - S_{Ag} - \Delta S^0$. These values have been listed in Table III, and are compared in Table IV with the previously available values.

TABLE II. *$E^{0\prime}_H$ as a function of temperature, cation, and molal concentration for T_R = 25°C*
$E^{0\prime}_H$ Values

T_H °C	0.00100m KCl	0.00108m CsCl	Electrolyte 0.0099m CsCl	0.100m KCl	1.0357m KCl
	v	v	v	v	v
25	0.22239	0.22239	0.22239	0.22239	0.22239
30	0.22309	0.22320	0.22333	0.22337	0.22338
35	0.22399	0.22407	0.22427	0.22434	0.22431
40	0.22499	0.22511	0.22518	0.22528	0.22516
45	0.22579	0.22585	0.22594	0.22614	0.22595
50	0.22628		0.22659	0.22685	0.22660
55	0.22678		0.22734	0.22763	0.22736
60	0.22737		0.22788	0.22829	0.22799
65	0.22796		0.22854	0.22890	0.22863
70	0.22875		0.22899	0.22941	0.22917
75	0.22949		0.22938	0.22985	0.22967
80	0.23033		0.22949	0.23027	0.23014
85	0.23071		0.22974	0.23066	0.23052
90	0.23090		0.23003	0.23099	0.23080

TABLE III. *Table of molal entropies (in entropy units)*

T_H	S^0 AgCl	S^0 Ag	From 0.1N KCl		From 0.001N KCl	
			ΔS^0	$S^{0\prime}_{Cl^-}$	ΔS^0	$S^{0\prime}_{Cl^-}$
°C	e.u.	e.u.	e.u.	e.u.	e.u.	e.u.
25	23.00	10.2	−4.52	17.3	−3.23	16.0
30	23.21	10.3	−4.50	17.4	−3.46	16.4
35	23.42	10.4	−4.41	17.4	−3.93	16.8
40	23.64	10.49	−4.16	17.3	−4.16	17.3
45	23.85	10.58	−3.72	17.0	−3.70	17.0
50	24.03	10.67	−3.44	16.8	−2.73	16.1
55	24.22	10.77	−3.26	16.7	−2.54	16.0
60	24.41	10.86	−2.93	16.5	−2.54	16.1
65	24.60	10.95	−2.54	16.2	−3.23	16.9
70	24.79	11.05	−2.19	15.9	−3.09	16.8
75	24.97	11.14	−1.99	15.8	−3.60	17.4
80	25.16	11.24	−1.87	15.8	−2.73	16.6
85	25.35	11.33	−1.66	15.7	−1.85	15.9
90	25.54	11.42	−1.48	15.6	−1.15	15.3

It is observed in Table III that above 35° to 40°C $S^{0\prime}_{Cl^-}$ decreases with increasing temperature. This might be possible in such a complicated environment as an aqueous solution, in which hydration forces vary with temperature, but could not occur with single materials by themselves.

The Soret Effect

It has been shown that the Nernst equation cannot completely account for the measured potentials of the Ag/AgCl thermogalvanic cell. The ion of the solute that is not involved in the cell reaction evidently influences the cell potential. A possible explanation may lie in the Soret effect. Eastman (6) implied that the system is in equilibrium only after the Soret effects have been fully established. He successfully corrected Richard's data (16) for the entropy of ion transfer, effecting agreement among $S^{0\prime}_{Cl^-}$ values obtained from electrolytes KCl and HCl at 25°C. However, since Soret coefficients are difficult to evaluate and since no data were found on the variation of these coefficients with concentration and temperature, only rough indications could be obtained here for the trend of Soret coefficient values with temperature at temperatures other than 25°C.

TABLE IV. *Comparison of $S^{0\prime}_{Cl^-}$ values at 25°C (in entropy units)*

Investigation	Electrolyte				
	0.1N KCl	0.01N KCl	0.01N CsCl	0.001N KCl	Unstated
This paper	17.3 e. u.		17.1 e. u.	16.0 e. u.	
Patrick (12)					18.25 e. u.
From Richard's data (16) Hg/Hg_2Cl_2 cell	17.85 e. u.	16.5 e. u.			
Buffington (2) (uncorrected)		18.5 e. u.			

Eastman's coefficients, when T_H is greater than 30°C, do not cause agreement between $S^{0\prime}_{Cl^-}$ values for the KCl and HCl electrolytes. From Fig. 2 it is noted that $\frac{dE}{dT}$ for 0.1N HCl decreases as T_H increases and even becomes negative at values of T_H above 70°C. Thus the Soret coefficient for H^+ must become continuously higher to bring about agreement with $\frac{dE}{dT}$ values for 0.1N KCl.

The Soret coefficient for potassium ion (6) is of a lower order of magnitude than that of hydrogen ion (0.5 as against 9.3 entropy units) and is therefore of secondary importance. In brief, the Soret effect appears, at least at present, inadequate to explain the values of E when HCl is the electrolyte.

The Effect of Solvent Entropy

Eastman's development of the theory of regions of interaction between solvent and solute indicates that the entropy of the solvent molecules is important in determining the measured E, and consequently $E_H^{0\prime}$ and $S^{0\prime}$. To a certain extent the influence of the solvent is reflected in the value of the activity coefficient of the electrolyte. Yet it is conceivable that the entropy of the solvent could influence in some other way the value of the electrode potential.

The Mechanism of Solvent Influence

The mechanism of solvent influence may be as follows. Consider the reaction $Ag \rightleftarrows Ag^+ + e$. There is evidence that Ag^+ is associated with (at least) two water molecules in complex formation (15). The stability of the Ag^+ in solution partly depends on the energy of binding of the water molecules. At a given temperature, if silver ions and chloride ions only are present in solution and AgCl is present in a solid phase in the vicinity of a silver electrode, the half-cell potential will be a function of the activity of Ag^+ in solution, which can be obtained from the solubility product K_{AgCl}. However when another electrolyte (KCl, NaCl, HCl, etc.) in appreciable concentration is added the concentration of Ag^+ may no longer be determined by the solubility product. The presence of the cations (and probably the anions also) alters the entropy of the solvent by their influence on Eastman's third region. They also exert a considerable influence on the aqueous silver complex, the hydrated silver ion. This influence may be due to competition for the bound waters and the entropy of the silver ion may be increased by the neutralization of electrical forces. The result may be that the aqueous silver ion is less stable. K_{AgCl} would no longer govern the amount of Ag^+ present, because K_{AgCl} assumes the Ag^+ in a definite statistically average state of hydration. The relative stability of Ag^+ is altered and it may combine with Cl^- more or less readily to form AgCl. The concentration of Ag^+ being changed, the silver electrode may become relatively more positive or negative. The strength of solvent binding is also a function of temperature.

Lack of Knowledge of Force Fields

Force fields in polar solutions are a provocative region of thought. It is difficult to give a quantitative picture because the magnitudes and directions of the complicated force fields and the extent of the various Eastman regions of influence are not known. However, the influence of the electrolyte and the solvent on the entropy of the ion involved in the cell reaction cannot be discounted. How much of this influence is reflected in the activity coefficient is difficult to predict. The above mechanism was presented because it predicts that $E_H^{0\prime}$ and $S^{0\prime}$, determined from the application of the Nernst equation, differ from the true theoretical $E_H^{0\prime}$ and $S^{0\prime}$, as this research indicated.

Briefly stated, entropy processes involving the solvent at the two half-cell temperatures may contribute to the somewhat anomalous thermogalvanic cell potential.

Summary

1. The thermogalvanic cell $(Ag/AgCl)_{T_1}/m MCl/(AgCl/Ag)_{T_2}$ was used to obtain values of $E_H^{0\prime}$ and $S_{Cl^-}^{0\prime}$ at temperatures between 25° and 90°C.

2. The influence of K^+ and Cs^+ and the effect of varying concentrations of electrolyte on these constants were found to be small but appreciable. The influence of H^+ was large.

3. The data and calculations indicate that standard thermodynamic relations for the reversible processes do not precisely determine $E_H^{0\prime}$ and $S_{Cl^-}^{0\prime}$. These values obtained by such relations should probably be corrected for mass transfer effects.

4. The Soret effects do not account completely for the variation in values of $E_H^{0\prime}$ and $S_{Cl^-}^{0\prime}$ when ΔT is greater than 10°C.

5. Entropy processes involving the solvent contribute to the thermogalvanic cell measurements.

6. Thermogalvanic measurements are useful if the temperature difference $T_H - T_R$ is not larger than 5° or 10°C, since a close approximate value of ΔS^0 for the half-cell reaction may then be obtained. Caution should be used in extending this value to estimate the magnitude of the maximum electromotive force developed by a much larger $T_H - T_R$, as in thermogalvanic corrosion situations in industry.

7. The method of equation (III) should not be applied to nonisothermal systems at pH's less than 4 or greater than 10, unless a correction for the high diffusion rates of H^+ or OH^- can be made. However, if properly applied, the thermodynamic method is valuable for corrosion purposes where extreme accuracy is usually not required. For thermodynamics, these $E_H^{0\prime}$ and $S^{0\prime}$ values obtained may be inadequate except as approximations, even when corrected by the Soret coefficients.

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Any discussion of this paper will appear in a Discussion Section, to be published in the June 1952 issue of the Journal.

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Production of Ductile Vanadium by Calcium Reduction of Vanadium Trioxide[1]

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ABSTRACT

Calculations were made to determine the heat of reaction of calcium with different oxides of vanadium. These calculations indicated better means of controlling the reaction. Ductile rod, wire, and sheet were fabricated from a powder produced by calcium reduction of V_2O_3. Fabrication furnished some information on working and annealing while other studies yielded physical property, purity, and microstructure data.

Introduction

Vanadium is eighth in order of natural abundance of those metals useful for structural purposes. In this respect, it ranks ahead of nickel and copper (1). It is one of the last of the rare metals to become available commercially, even in limited quantities, in a fabricated form.

This metal was first indicated to be ductile by Von Bolten (2), who produced malleable beads in 1905 by the dissociation of V_2O_3 at high temperatures. Saklawalla (3) summarized the properties of the metal.

Marden and Rich (4) reported the production of ductile vanadium in 1927 by the reduction of V_2O_5 with calcium and calcium chloride[2]. They also gave a good summary of the prior art. Following their publication, the literature on pure vanadium has been sparse.

Van Arkel (5), in a summary of his work on the "hot wire" process, mentions making vanadium from the iodide by thermal dissociation. Dorning and Geiler (6) reported the preparation of vanadium powder by hydrogen reduction of vanadium trichloride. A reduction time of 80 hr was required to yield 2 grams of powder from 7 grams of the trichloride.

Morette (7) reduced the various chlorides of vanadium with magnesium, and obtained a metal powder of 99 per cent vanadium, or better, but does not mention consolidation of the product into massive metal.

Kroll (8) has concluded that the reduction of vanadium oxide with carbon is not practical. He also studied (9) the reduction of oxides of vanadium with calcium and calcium chloride and obtained a product which was hot malleable. McKechnie and Seybolt (10) produced cold ductile vanadium in massive form by the reduction of the pentoxide with calcium. Kinzel (11) announced the production of vanadium in massive form, but no mention of the method used was made.

General Considerations

It appeared that the most promising methods for development would be those involving the reduction of the chloride or oxide of vanadium with magnesium or calcium, respectively. Magnesium is considerably cheaper than calcium, but handling vanadium chloride is a difficult operation. The chloride should be oxygen-free, and since both the chloride and oxychloride are volatile, fractional distillation is necessary for their separation. There is sufficient difference in their boiling points to permit such a separation, but the vapors form a fog which is difficult to condense. Furthermore, the unstable nature of the volatile chlorides probably would result in the attack of any metal system not resistant to free chlorine. The chlorides of vanadium are also extremely hygroscopic, precluding exposure to the atmosphere. Magnesium should reduce vanadium oxide, but the problem of removing the magnesium oxide formed in the reaction appears difficult.

The oxides of vanadium may be prepared in a pure stable form with comparative ease, and the production of ductile vanadium beads by calcium reduction of the pentoxide was shown to be possible by Marden and Rich (4). They obtained a product composed of some metal powder and some fused beads which

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[2] The process of Marden, *et al.*, was patented abroad in the name of Cachemaille as agent.

varied in size up to ¼ in. diameter. However desirable such beads may be, and some were rolled into wire, it is not the type of product adaptable to the formation of massive metal by powder metallurgy which was one objective of the development to be described.

To yield fused beads, the temperature of the reaction mass must exceed the melting point of vanadium during the reduction cycle. This is possible because the reaction is strongly exothermic. To obtain a uniformly fine powder which could be fabricated by pressing and sintering, it was necessary to control the temperature of the reaction so that the melting point of the metal would not be exceeded. The quantities of reactants specified by Marden and Rich (4) for

$$V_2O_5 + 5Ca = 2V + 5CaO \qquad (I)$$

included 2.8 moles of $CaCl_2$ and 2.8 moles excess of Ca. With these quantities the heat of the reaction as calculated from standard heats of formation is $\Delta H_{298} = -321.5$ kcal/mole V_2O_5. The theoretical maximum temperature of the charge may be calculated after the manner of theoretical flame temperatures using heat capacities (12) known to at least 900°C and which may be approximated at higher temperatures. This was estimated to be about 2400°C. This temperature may be held down by increasing the heat capacity of the charge by the addition of further calcium or calcium chloride as diluents. Such additions, however, greatly reduce the capacity of a given reaction vessel. Moreover, the low melting point of V_2O_5 (670°C) no doubt increases the speed of the reaction and may contribute otherwise to bead formation.

A general solution to these problems appeared to be in the substitution of a lower oxide of vanadium as V_2O_3 for the pentoxide. The melting point of V_2O_3 is high, and the heat of reaction is $\Delta H_{298} = -125.1$ kcal/mole, considerably lower than that obtained in the case of the pentoxide. Thus the heat liberated is about one third of that obtained by use of the pentoxide per mole vanadium produced. This also permits the amount of vanadium per unit charge to be increased greatly. The reaction in this case becomes

$$V_2O_3 + 3Ca = 2V + 3CaO. \qquad (II)$$

The reactants include 1 mole of $CaCl_2$ which is recovered and 3 moles excess of Ca.

For reaction (II), the maximum temperature reached was calculated to be about 1900°C which is a little above the melting point of the metal. The reaction rate may, however, be somewhat slower as the trioxide does not melt below 1965°C.

Methods and Results

Experimental Reductions

Since it was desired to follow the techniques developed in this laboratory for such operations, wherein the reduction is carried out in a Vycor-glass system, Fig. 1, it was essential that the reaction be controlled. It was also found that the ratio of reactants has an important bearing on the quality of the product obtained.

Calculations were made to determine the amount of calcium chloride which would be necessary to avoid a violent reaction. It was found that 4 moles of calcium chloride would limit the theoretical maximum temperature to 1200°–1300°C. In the experimental work, the first reductions were run using a mole ratio of $CaCl_2/V_2O_3$ of 4/1. This did not produce a satisfactory powder. On successive runs this ratio was decreased until it was determined that a safe limit was reached at a mole ratio of 1/1. Excess of

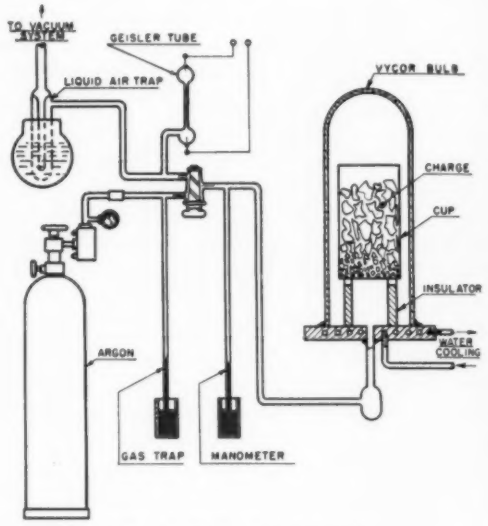

Fig. 1. Reduction apparatus

calcium over theoretical of 100 per cent was used in all cases. It was with this ratio that the first workable metal was produced. The maximum temperature reached was near that calculated (1900°C), as confirmed by the presence of a few small beads in the charge.

It is interesting to note that bead formation, which constituted a very small fraction of the charge, revealed three types of beads which varied in hardness and ductility. Photomicrographs of such beads are shown in Fig. 2. The Vickers microhardness readings on the solid beads averaged 200 V.P.N.[3] for the ductile and 724 V.P.N. for the brittle. This is shown by the size of the indentations at the same loading. In addition, a third spongy type of bead was also noted as shown by the porous structure at the far right in the photomicrograph.

Having established a method by which a good powder could be produced, successive batches were

[3] Vickers pyramid number.

made from which cold ductile bar, wire, and sheet have been fabricated.

An outline of the process used for the preparation of vanadium powder and its consolidation into mass metal is given below.

Powder Preparation

The starting materials used in vanadium preparation are V_2O_5 (C.P.), distilled calcium, which should contain not over 100 ppm of nitrogen, and 99.5 + per cent assay $CaCl_2$.

The first step is reduction of V_2O_5 to V_2O_3 at 600°C in hydrogen. The reaction is relatively fast and is conveniently carried out in a tube furnace using nickel or stainless steel boats. A brownish black product is obtained according to the following reaction:

$$V_2O_5 + 2H_2 = V_2O_3 + 2H_2O. \qquad \text{(III)}$$

The product is ground to pass a 100-mesh Tyler screen and mixed with cut calcium, approximately $\frac{1}{8}$ in. mesh, and powdered calcium chloride in the proportion V_2O_3, 1 mole; Ca, 6 moles; and $CaCl_2$, 1 mole. The charge is then placed in the iron container, Fig. 1, which has been previously lined with calcium or magnesium oxides to prevent iron contamination during the reduction cycle.

Satisfactory cup linings have been produced by painting, or spraying a mixture of magnesium oxide and nitrocellulose binder on the inner surface of the container and then heating in air to remove the binder. Linings have also been formed by inserting a thin cylinder into the container leaving an annular space which is filled with Ca or Mg oxides. The bottom of the container is also covered with an oxide layer. After insertion of the mixed charge the cylinder is withdrawn leaving a protective layer of the oxide between the charge and the container.

The charged container is supported inside the Vycor bottle. The latter rests on the brass tubulated plate and is sealed thereto with vacuum wax. The Vycor bulb is evacuated to 100 μ or less, 99.7 per cent argon gas admitted to a pressure of approximately 0.8 atm, and the stopcock closed. The charge container is heated by means of high-frequency coils (not shown in the drawing) surrounding the Vycor cylinder, and after the reaction mass fires the container is maintained at approximately 1000°C for 1 hr, sufficient to complete the reduction. Temperatures are read with an optical pyrometer sighted on the outside of the container.

When cold, the charge container is removed and leached with 40–50 per cent acetic acid. The reaction mass is cooled during leaching by the use of cooling coils, or a stainless steel vessel may be used which is placed in a cooling tank. After the reaction is complete, the vanadium powder is washed several times by decantation with water to remove dissolved salts and acid. The powder is then recovered by filtration and vacuum drying at 40°–50°C. The over-all yield of powder was 80 to 85 per cent discarding fines lost in the washing operation and based on an initial charge of 200–500 grams of V_2O_3.

Vanadium powder prepared thus is somewhat unstable. If not immediately pressed and sintered, deterioration may occur as evidenced by the formation of a green discoloration. The powder may be stabilized by heating in a vacuum to 400°C in a system capable of maintaining an ultimate pressure of 0.1 to 1 μ. During such treatment a large volume of hydrogen gas is evolved. After pumping down to the pressures referred to, the powder may be stored for reasonably long periods without apparent deterioration.

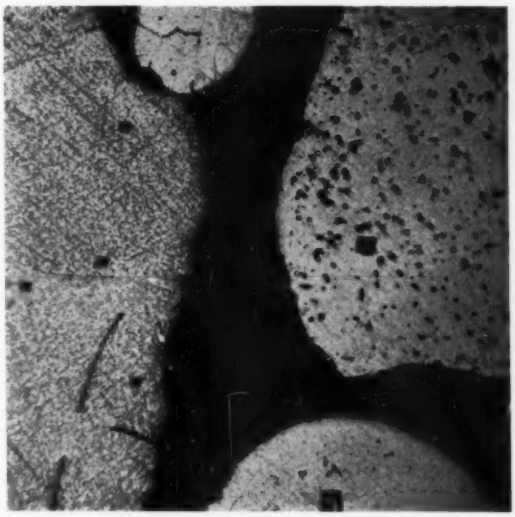

FIG. 2. Vanadium beads

Thoroughly degassed powder may become activated and fire on exposure to the air. This can occur even though the powder is cooled to liquid air temperatures prior to exposure. In any case, there appears to be evidence of an exothermic reaction of air or oxygen with the powder on exposure to air which no doubt results in slight oxidation. It is possible that these difficulties can be overcome by hydriding the powder prior to exposure and then later removing the hydrogen. This is easily accomplished at relatively low temperatures. In view of the unstable character of the powder it is best, therefore, to convert it into mass metal as soon as possible.

Ingot Preparation

The activity exhibited by vanadium powder toward oxidation when exposed to air is also evident in some cases in pressed and vacuum sintered ingots. It has been found possible to form ingots by pressing the powder in steel dies at 15–20 tons/in^2. and then

sintering in vacuo. Ingots sintered for 10–15 hr at 1000°C have a relatively low density and react with air, becoming warm upon initial exposure. On treating up to 1400°–1500°C for 1–2 hr, the density increases to about 98 per cent of maximum and the ingots exhibit no activity toward air. It is desirable, therefore, to sinter directly from the green compact to maximum density. A vacuum sintering furnace for this operation is shown in Fig. 3. This comprises a Vycor cylinder (A) which rests on a water-cooled, tubulated brass plate (B), hermetically sealed with vacuum wax (C). The tubulation (D) serves for evacuation of the furnace through a conventional high vacuum exhaust unit.

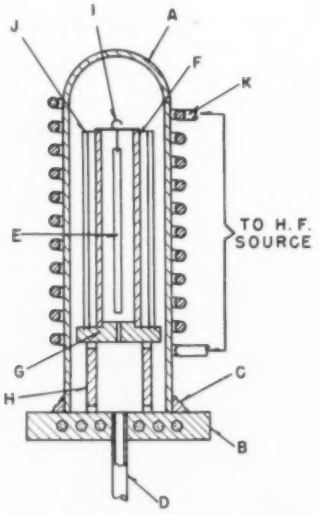

FIG. 3. Vacuum sintering furnace

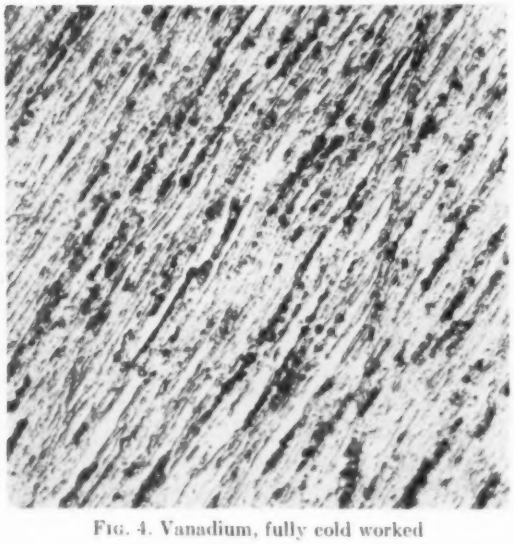

FIG. 4. Vanadium, fully cold worked

The pressed bar (E) is suspended centrally in the molybdenum tube (F) which rests on the molybdenum block (G) set on insulators (H). The bar is suspended by tantalum wire (I) and held in position by the molybdenum cover (J). The molybdenum tube (F) is surrounded by two split molybdenum shields which reduce radiation to the Vycor bottle during operation. The source of power is a 50 kva, 10,000 cycle motor-generator set and the inner cylinder of molybdenum is heated by activating the coils (K). The furnace has been used for sintering at temperatures up to the point at which the vapor pressure of molybdenum becomes a limiting factor.

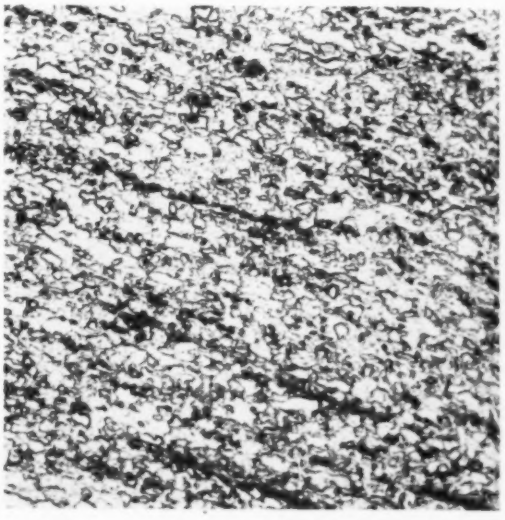

FIG. 5. Vanadium annealed at 750°C for ½ hr

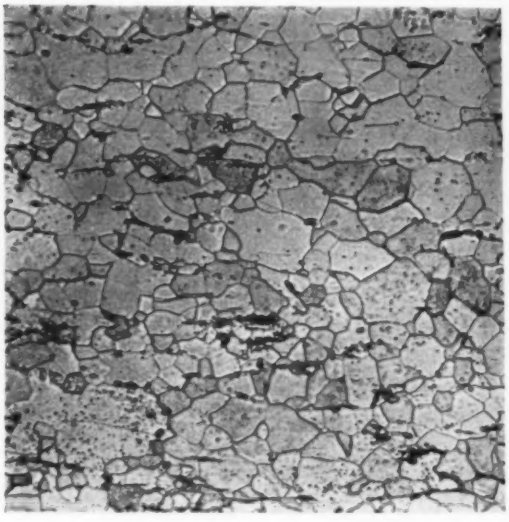

FIG. 6. Vanadium annealed at 1000°C for ½ hr

Fabrication of Vanadium

Vanadium produced as described may be fabricated into ductile wire or sheet by working schedules similar to those used in current practice for zirconium and titanium.

Initial breakdown is accomplished by heavy passes about 25 per cent reduction in area, the metal being heated in argon to 600°C between passes. The use of argon may not be necessary up to this temperature because only mild surface oxidation seems to occur. Rolling is continued with gradual reduction in drafts to a minimum of 10–15 per cent per pass until annealing becomes necessary, usually at about 50 per cent total reduction in cross-sectional area. Samples have also been hot forged and rolled inside a protective iron sheath up to 1000°C. The metal may be completely annealed in vacuo at 850°C for 1 hr.

Fig. 4 shows the microstructure of the metal in the fully cold-worked state at maximum hardness (V.P.N. 344). Fig. 5 shows the same material after annealing in vacuo at 750°C for ½ hr. Fig. 6 shows the structure obtained by annealing the cold-worked material for ½ hr at 1000°C. It is to be noted that the material treated at 750°C is considerably equiaxed and that considerable grain growth occurred in the sample annealed at the higher temperature.

Properties of Vanadium

In determining physical properties of rare metals as prepared by a process similar to that described, it is the properties of alloys which are in fact determined. This is particularly true of metals which dissolve appreciable quantities of oxygen, nitrogen, or both as do Zr, Ti, and V. The amount of such gases in solid solution has a very pronounced effect on such properties as hardness, ductility, and tensile strength. In general, these gases result in increased hardness and tensile strength, and decreased ductility.

The only satisfactory method for determining oxygen in vanadium at the present time appears to be the vacuum fusion technique, although insufficient data have been collected to evaluate thoroughly the accuracy of the method. A typical analysis in per cent by weight is: 0.05 Ca, 0.05 C, 0.01 Fe, 0.1–0.25 O_2, 0.01–0.015 N_2, and 99.7–99.8 V.

Limited physical tests on such materials indicate an ultimate tensile strength of 100,000 psi for annealed vanadium and 140,000 psi for work-hardened metal. The corresponding hardness values were 230 V.P.N. for the annealed and 330 V.P.N. for the work hardened. The corresponding elongation for fully annealed samples of 0.10 in. diameter and 0.5 in. gauge length was 23 per cent; for the work-hardened material, 0.05 in. diameter and 0.5 gauge length, 3 per cent. Such figures for tensile strength and elongation are for metal containing appreciable oxygen and nitrogen. As the purity of the metal is improved a considerable drop in tensile strength and increase in elongation may be expected.

Vanadium is very susceptible to hydrogen embrittlement which can be removed by heating in vacuum up to 400°C.

No unusual difficulty was experienced in machining either the annealed or work-hardened metal.

Summary

A process for the production of high purity vanadium powder by the reduction of vanadium trioxide with calcium is described, as are the forming, treating, and mechanical working of vanadium compacts. Soft, ductile vanadium rod, wire, and sheet have been produced following powder metallurgy practice.

The physical properties of vanadium appear to be largely dependent upon the oxygen and nitrogen content of the metal. Metal containing oxygen in the range 0.1–0.25 per cent, and nitrogen 0.01–0.04 per cent, shows a tensile strength in the annealed condition of approximately 100,000 psi. The corresponding elongation for 0.1 in. diameter rod and 0.5 in. gauge length was 23 per cent.

Because of limited data and uncertainties in the determined oxygen values, the figures given are only indicative of the order of strength and ductility of a very high purity product. With further improvement in the oxygen or nitrogen elimination, the tensile figures may be expected to decrease and the values for elongation to increase.

Any discussion of this paper will appear in a Discussion Section, to be published in the June 1952 issue of the Journal.

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Calcium Phosphate Phosphor Activated with Cerium and Manganese[1]

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ABSTRACT

The useful deep red emission of $Ca_3(PO_4)_2$:(Ce,Mn) phosphors is obtained over a rather wide range of activator concentrations, and with materials prepared by different methods. Nearly all phosphor characteristics, except for the red emission band, closely parallel those for the $Ca_3(PO_4)_2$:Ce parent phosphor. The ratio of sensitizer (Ce) atoms to emitter (Mn) atoms is by one or two orders of magnitude larger than in most other sensitized phosphors. Partial substitution of calcium by other elements, and excitation at higher temperatures, lead to shifts in peak emission toward shorter wavelengths and to improved temperature stability of the phosphors, notably those with sodium as substituent. An optimum effect is obtained with a mole ratio of Na:Ce = 1:2, which approaches the 1:1 requirement of Kroeger's simple theory of stabilization.

Introduction

Calcium phosphate activated with cerium and manganese has recently gained some technological importance as a red emitting phosphor in fluorescent lamp applications. It was the first red phosphor of acceptable efficiency to permit the design of fluorescent light sources having emission spectra that extend farther into the deep red range than had previously been possible. A general emission curve of this type phosphor has been published (1). Certain additional characteristics of interest will be described in this paper.

The phosphor belongs to the general class of double-activated or "sensitized" phosphors which have become of great technological importance during the last few years. The material may be represented by the formula, $Ca_3(PO_4)_2$:(Ce,Mn). Manganese is the principal useful emitter in the phosphate base, while the function of cerium is that of an element now commonly, though not rigorously, called a "sensitizer." However, the amount of sensitizer in this phosphor is unusually large, in fact one or two orders of magnitude larger than it is in most other sensitized phosphors now known. In common with similar phosphors, the sensitizer contributes significantly to the total fluorescent emission.

Preparation

A number of different methods are suitable for the preparation of the phosphor. For example, a mixture of calcium, cerium, and manganese phosphates may be coprecipitated from aqueous solutions of the respective nitrates with a solution of ammonium phosphate. Except for small amounts of calcium the precipitation is nearly quantitative when carried out in hot solution. After filtration and drying, the powder is fired at 1200° to 1300°C in an atmosphere of steam and hydrogen, and then cooled in the same atmosphere.

A second method consists of preparing a dry powder mixture of calculated amounts of $CaHPO_4$, cerium carbonate or oxalate, manganese carbonate or phosphate, and calcium carbonate. This mixture is fired once or twice in air at 1200° to 1300°C and then cooled in an atmosphere of hydrogen plus nitrogen or hydrogen plus steam. Other methods of preparation, or a different choice of raw materials, have also given good results.

The formulation of a phosphor batch and the firing conditions are mutually dependent. They must be so chosen that the fired phosphor approximates the composition of the triorthophosphate. Cerium and manganese phosphate form solid solutions with calcium phosphate, as found by x-ray diffraction. Hence cerium and manganese in activator concentrations can substitute in equivalent amounts for calcium. While compounds with excess of either acid or base oxide fluoresced less brightly when measured as dry powders, some of them showed advantages in the lamp application over the theoretical triortho compounds. When fired at temperatures above 1100°C the resulting phosphor phase showed the α triorthophosphate structure; below 1100°C it was β triorthophosphate. The fluorescent emissions of the two phases appeared to be identical, but the intensity of emission from the α phase was greater.

The emission of phosphors with excess base oxide or acid was identical under 2537 Å excitation. Under cathode ray excitation, however, significant differences in emitted color were observed, materials with

[1] Manuscript received May 16, 1951. This paper prepared for delivery before the Washington Meeting, April 8 to 12, 1951.

excess acid fluorescing yellow-orange to orange, while triortho or more basic compounds fluoresced red.

The conversion of $CaHPO_4$ into triorthophosphate by firing in steam and hydrogen has been discussed before (2). In the second method, outlined above, the formation of triorthophosphate must be assured by solid phase reaction with suitable amounts of the base oxides or oxide donors used. As already indicated, all three oxides, CaO, Ce_2O_3, and MnO, must be counted as base oxides to satisfy the stoichiometric base requirement of a given amount of P_2O_5 introduced as $CaHPO_4$ or $MnHPO_4$.

Cerium is effective in the phosphor when present in the trivalent Ce^{3+} state. When dissolved in the calcium phosphate matrix, trivalent cerium appears to be stable in air both at low and at very high temperatures. Phosphors exposed to oxidizing atmospheres in intermediate temperature ranges fluoresced much less brightly, presumably due to oxidation of the activator. Hence firing and cooling, or at least cooling, of the phosphors in definitely reducing atmospheres was necessary. Heating of bright phosphors in oxidizing atmospheres led to considerable deterioration of brightness, when remeasured at room temperature.

The brightness loss of air-heated phosphors is not merely a surface effect. This was deduced from brightness measurements of air-heated vs. hydrogen-heated phosphors which were ground in acetone for a specified length of time in a ball mill. Had the brightness loss been only a surface effect, then the brightness of the two milled samples should have been nearly the same despite the original brightness differential of the unmilled phosphors. Actually, the samples showed the same relative brightness *loss* after milling, which would indicate that the deterioration had spread through the whole interior of the phosphor crystals, each sample then showing the normal loss due to mechanical grinding.

General Characteristics

The spectral sensitivity of the phosphor, according to measurements of Barnes of this Laboratory, shows qualitatively the same picture (Fig. 1) as the parent phosphor containing cerium alone as single activator (see Ref. 2). Two broad and overlapping excitation bands are prominent, with maxima at about 2650 and 3150 Å, the longer wavelength band being the stronger of the two as in the case of cerium alone. The sensitivity at 2537 Å is only about 74 per cent of the peak sensitivity at 3150 Å. This is in contrast to Kroeger's samples (3) which showed the effectiveness of the two excitation bands in reverse order. The single activated $Ca_3(PO_4)_2$:Mn phosphor, on the other hand, is nearly transparent to radiation from about 2300 Å to the visible range, and so does not fluoresce when irradiated with these wavelengths. Shorter wavelength ultraviolet, however, is absorbed and leads to fluorescence as observed already with the mercury radiation of 1849 Å. Thus all excitation of the double-activated phosphor by 2537 Å radiation is due to the cerium which is the primary absorber of this radiation.

Under 2537 Å excitation, the double-activated phosphor shows a well-defined two-band emission (Fig. 2). The red band is due to divalent manganese as principal emitter and has a room temperature peak at about 6500 Å. The same red band may be obtained

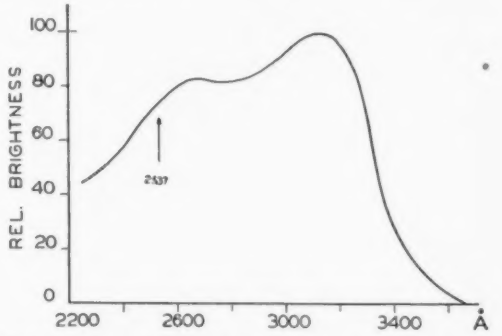

Fig. 1. Spectral sensitivity of $Ca_3(PO_4)_2$:(Ce,Mn) phosphor with strong red emission.

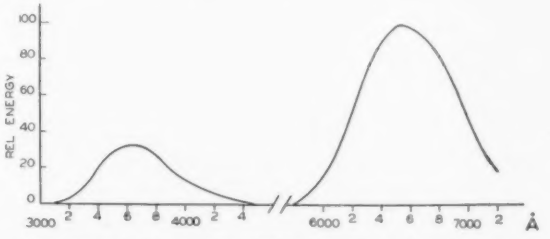

Fig. 2. Emission of $Ca_3(PO_4)_2$:(Ce,Mn) phosphor under 2537 Å excitation at room temperature.

by cathode ray excitation of the single- or double-activated phosphors with manganese. Variation of the cerium and the manganese concentrations in the phosphors has given the following results. Over a wide range of concentrations, from about 0.1 to 5 per cent by weight of MnO, the position and shape of the emission bands are substantially independent of the manganese concentration. Their relative intensities vary, such that the sum of energies in the two bands remains substantially constant. However, for each manganese concentration there is an optimum concentration of cerium to give the greatest total brightness without affecting the shape or position of the red band significantly. This optimum, while itself rather broad, shows a tendency in the direction of higher cerium contents for higher manganese contents.

The brightest phosphors were obtained in the general range of about 2 to 3 per cent by weight of MnO and about 12 to 16 per cent by weight of Ce_2O_3 in the final phosphor. As already mentioned, this is an unusually high concentration for a "sensitizer." For the median concentrations this represents about 0.035 moles MnO for 0.085 moles of cerium (Ce), or about 0.4:1 for the mole ratio. This ratio of 0.4:1 for emitter to sensitizer atoms in this phosphor compares with about 10 to 50:1 for calcium silicate activated with manganese and lead, and similar ratios for manganese to antimony in common calcium halophosphates. Thus the necessary amount of sensitizer in the red phosphor is one or two orders of magnitude larger than in other and even more efficient sensitized phosphors, suggesting perhaps a different mechanism of sensitization.

This is also suggested by a study of brightness changes with excitation at low temperatures. The intensity of the cerium emission in $Ca_3(PO_4)_2$:Ce shows only a slight decrease at the temperature of liquid air. On the other hand, when $Ca_3(PO_4)_2$:(Ce,Mn) phosphor is cooled to that temperature, the red emission due to the Mn decreases sharply, while the ultraviolet emission due to Ce *increases* to a value of two or three times the intensity at room temperature. This is in contrast, for example, to the sensitized $CaSiO_3$:(Pb,Mn) phosphor whose ultraviolet emission decreases slightly in intensity at low temperature just as in the single-activated $CaSiO_3$:Pb phosphor.

The quantum efficiency of the red phosphor was determined by the method of Thayer (4). A value of 62 per cent was calculated for the red band and of 12 per cent for the ultraviolet band, bringing the total to about 74 per cent. This is roughly 10 per cent higher than the value reported by Kroeger (3).

When compared with most other phosphors which are technologically useful, the efficiency of the red phosphor is of somewhat lower order. An obvious cause for low brightness is undesirable impurities in the phosphor, whose effect was therefore studied extensively. Known amounts of impurity elements were added to phosphor preparations made according to method I. Most of these elements, such as iron, were found to reduce phosphor brightness as expected. Some elements, however, such as zirconium and samarium, were found to poison the emission to a considerably greater degree than was expected from their concentration. Thorium was expected to increase the efficiency as in the parent phosphor with cerium alone (2). However, no improvement of the red efficiency was found with the introduction of thorium.

By extrapolation of brightness data it was concluded that the brightness of the red phosphor could not be increased significantly by going to extremes in the purification of the raw materials. The same experiments, interpreted from a different point of view, indicated that the brightness of the red band could not be further increased with the introduction of third "activators." Still puzzling, however, are significant and consistent brightness differentials due to cerium compounds obtained from different commercial sources. Impurities, if any, that might have caused reduced brightness quite reproducibly, could not be traced analytically.

Modified Phosphors

Attempts were made to modify the phosphor emission or increase its brightness, through partial substitution of calcium with equivalent amounts of its homologues and other substituents. Most of these phosphors were prepared according to method II. The substitutions could generally be made only to the extent of a few mole per cent without risk of excessive sintering of the material or actual brightness losses. An exception was strontium which could be introduced in fairly large amounts such as 20 mole per cent or more. The strong fluxing action of some of the substituents necessitated a lowering of the firing temperature to about 1160°C or lower. Most substituents produced a slight shift in the peak position of the red band, as shown in column 2 of Table I for room temperature measurements.

TABLE I

Substituent	Peak emission (Å) (2537 excit.)	g Oxide per 100 g phosphor	I_{300}/I_{25} (2537 excit.)
None	6500	—	18%
Na	6500	0.4	59
Na	6500	1.3	61
Na	6500	2	30
K	6490	.5	50
Li	6480	.35	57
Zn	6470	1.8	30
Al	6450	2.3	
Mg	6450	.67	
Ba	6440	8.6	54
Sr	6420	13.5	

No significant changes in the relative intensities of the ultraviolet and red bands were found with the introduction of substituents for calcium. Likewise, the decay constant of the long monomolecular manganese decay was not altered. For example, the de-

cay of phosphors with and without sodium was the same at room temperature.

Temperature Dependence

Kroeger (3) has already reported a shift of the red emission peak toward shorter wavelengths with increasing temperature of excitation, and an attendant broadening of the band. We find that the peak shifts approximately linearly, from 6600 Å at liquid air temperature to about 6200 Å at 400°C, the highest temperature at which fairly reliable measurements could be made with 2537 Å excitation (Fig. 3). In some of these experiments the phosphors were kept in an atmosphere of nitrogen or hydrogen, in others they were heated in air at a rapid rate. While the intensities were lower for the samples heated in air, for reasons given above, the position and shape of the emission curves were not affected by the loss of brightness.

The data for Fig. 3 were obtained by recording spectral distribution curves of a sample at a certain setting of the amplifier voltage for the phototube, without disturbing the geometry of the arrangement during the heating cycle. The phosphors were excited by radiation from a well-seasoned germicidal lamp giving constant output. Spectral distribution curves were drawn at temperatures as closely as possible to the temperatures of the cycle: Room T—100°C—400°—300°—200°—100°C—Room T, the total run requiring less than 30 minutes. The height of the recorded curves at the peak positions was taken as a measure of intensity. Duplication of the first 100° intensity, at 100° C on the down cycle, or deviation from it, was taken as a measure of the permanent damage done to the phosphor as a result of exposure to hot air. Exclusion of air was not quite complete and some brightness loss always occurred. In the best runs the resulting loss was of the order of 5 per cent. The temperature was measured with a small thermocouple dipping into the phosphor surface. Eddy drafts over the phosphor probably caused some deviation of true phosphor temperatures from those recorded and will explain the fact that the points of Fig. 3 do not lie more closely to the line drawn.

The curves show a gain of about 0.1 per cent per degree C for the broadening at the half-width level. This growth occurs principally on the short wavelength side of the emission curve and hence lends some strength to otherwise meager evidence for a possible doublet nature of the red band, which could account for the shift of peak position with temperature.

Fig. 4 shows typical curves obtained by plotting the peak intensities of the recorded curves against temperature. The plot shows a slope of about 2 for the unmodified phosphor, as well as for powders made with several substituents for calcium. The alkalies, and particularly sodium, however, make an interesting exception. Increasing amounts of sodium, up to a content of about 2 per cent by weight expressed as Na_2O, reduce the slope to about 1, which denotes considerably greater temperature stability. This is also shown in the last column of Table I which gives the brightness of some substituted phosphors as measured at 300°C in terms of their respective room temperature brightness. Accordingly, the introduction of sodium in an amount equivalent to about 1.3 per cent Na_2O produced an optimum brightness. It improved the relative brightness of the red band at 300°C better than threefold, compared with the unmodified phosphor, under 2537 Å excitation. At higher temperatures the relative gain becomes even greater.

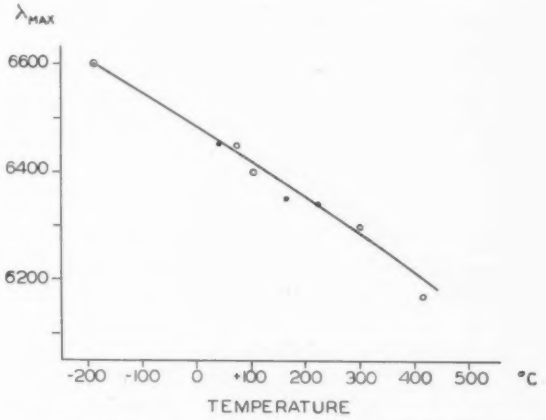

Fig. 3. Shift of peak emission with temperature under 2537 Å excitation.

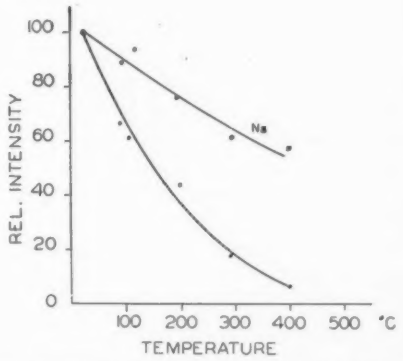

Fig. 4. Temperature dependence of peak emission for phosphors with and without sodium under 2537 Å excitation.

The response of $Ca_3(PO_4)_2$:(Ce, Mn) phosphors to 3650 Å radiation is practically nil at room temperature. It becomes somewhat stronger as the temperature is increased but attains only inconsequential intensity. The phosphors with added sodium, how-

ever, show a considerable gain in intensity at high temperatures, such that the brightness at 300° to 400°C is sufficiently high to become practically useful. An attendant color shift toward shorter wavelengths is even stronger than with 2537 Å excitation. At 500°C the phosphor with sodium was brighter under 3650 Å radiation than any other phosphor that we have examined. The optimum concentration of sodium for 3650 Å excitation lies slightly higher than for 2537 Å excitation. The combination of fairly high sensitivity to both 2537 and 3650 Å excitation at high temperatures makes the phosphor attractive for use in the color correction of high pressure mercury lamps. Indications are that the presence of sodium does not accelerate or produce any solarization of the phosphor by exciting radiations down to 1849 Å.

Discussion

It appears to be typical of all sensitized phosphors now known, that a comparatively large part of the total fluorescent energy (some 10 to 20 per cent or more) occurs as unmodified emission of the sensitizer element itself. The emission of the sensitizer lies always toward the short wavelength side of the emission by the principal emitter. The intensity of the sensitizer emission is governed by the concentration of the principal emitter element. Except for intensity, the emission is identical with that of phosphors containing the sensitizer element alone as single activator in the respective base material. This refers to the spectral energy distribution of the sensitizer band as well as to its unaltered decay characteristics as shown by Studer (5). Thus the essential characteristics of the lead emission in calcium silicate, of the antimony emission in apatites, and of the cerium emission in the present case, are retained even with the introduction of additional manganese and, in the latter phosphor, sodium. From a practical viewpoint it would be desirable to suppress the sensitizer emissions that do not lie in the visible as completely as possible, and to make the balance of energy available in form of greater intensity of the principal activator's emission. However, attempts in this direction have so far failed to upset the ratio of energies in the two bands appreciably. Neither changes in matrix composition nor the introduction of third activators have improved the efficiency of the principal emission band.

It seems to be further characteristic of double-activated phosphors that the color of their fluorescent emission is primarily determinded by the concentration of the principal emitter and the attendant degree of distortion of the base lattice, and only to a much smaller degree by the concentration of the sensitizer. The latter determines chiefly the efficiency of light emission by the principal emitter. However, the range of sensitizer concentrations beyond which efficiency declines is usually very broad. It may vary over a range of 2:1 without affecting the principal emission materially. In the present case, for example, a change of the cerium content from 8 to 20 per cent will produce phosphors whose brightness varies by not more than about ±5 to 10 per cent.

The improvement of the $Ca_3(PO_4)_2$:(Ce,Mn) phosphor with the introduction of alkalies, especially sodium, is somewhat puzzling. X-ray diffraction data obtained with recording instruments do not indicate the appearance of new phases, only a very slight distortion of the lattice and a definite increase in intensity and sharpness of some of the $Ca_3(PO_4)_2$ lines, due to the introduction of sodium. It may be concluded that the sodium atoms are distributed in solid solution in the phosphate base. In the absence of new phases, and in view of the unaltered decay characteristics of the phosphor, the improved temperature stability and the gain in 3650-response must be attributed to other causes.

It might be speculated that a crystal lattice having fewer vacancies or defects and showing some closer packing may also show greater temperature stability. This, as well as the incorporation of sodium in the phosphor, would be possible according to a picture first advanced by Kroeger for sulfides (6). If cerium ions of charge 3+ replace calcium ions of charge 2+ in the phosphate lattice, some interstitial positioning must take place or occasional lattice vacancies must be created in order to maintain the balance of charge. The situation is similar to the case of solid solutions of Ce_2S_3 in SrS (7) where large amounts of trivalent Ce can substitute for divalent Sr with the creation of lattice defects. (Calcium and manganese ions are fully interchangeable in the phosphate lattice.) If, however, additional monovalent ions could be introduced along with the trivalent cerium ions, then two ions of total charge 4+ (one ion of charge 3+ and one ion of charge 1+) would replace two calcium ions of charge 2 (2 plus 2 = 4+), without creating the need for interstitial ions or vacancies. Hence an optimum effect should be obtained with the introduction of equal numbers of mono- and trivalent ions.

Obviously, a condition for the effectiveness of this scheme is that the monovalent ions do not poison the fluorescent emission, a condition which the alkalies seem to fulfill in this case. With the double-activated phosphate an optimum effect was obtained with a concentration of sodium equal to about 1.3 per cent Na_2O. This corresponds to about 1 atom of sodium for each two atoms of cerium. It is thus apparent that charge alone is not the only determining factor, and that other effects such as polarization and type

of bonding must receive greater consideration. However, these results seem to support the theory at least qualitatively.

Admittedly, the scheme requires the presence of an unusually high concentration of vacancies just as in the case of the system SrS-Ce_2S_3. Since the room temperature emission and brightness of phosphors with and without sodium are identical, no major differentials of structure should be expected with the introduction of sodium, at least so far as the actual light emitting centers are concerned. The x-ray data seem to confirm this. One might have to introduce the additional assumption that only a small proportion of the total activator atoms takes part in the acts of absorption and emission (or energy transfer), and that it is only these active atoms which are charge-balanced by sodium to show the increased temperature stability. Of course, the whole hypothesis is valid only if the phosphor is truly a single phase material.

ACKNOWLEDGMENT

The authors are indebted to Dr. F. J. Studer and Mr. E. S. Steeb, Jr., for some of the measurements reported.

Any discussion of this paper will appear in a Discussion Section, to be published in the June 1952 issue of the JOURNAL.

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An Arsenic-Activated Zinc Sulfide Phosphor[1]

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ABSTRACT

The addition of small amounts of arsenic to zinc sulfide produces a phosphor which has three emission bands when excited by ultraviolet light or cathode rays. The blue band at 4650 Å is the one that is also present in unactivated zinc sulfide phosphors. The other two bands at 5200 Å and 6200 Å are due to the presence of arsenic. The relative intensity of the various bands depends on the concentration of arsenic, the atmosphere in which the phosphor was fired, the mode of excitation, and the temperature during excitation. By a proper adjustment of the arsenic concentration, phosphors can be prepared, the emitted light of which appears white.

INTRODUCTION

McKeag and Ranby (1) have described a phosphorus-activated zinc sulfide phosphor having two emission bands. The relative intensities of the bands were found to depend on the phosphorus concentration in the finished phosphor as well as the mode of excitation. Thus by a suitable adjustment of the phosphorus concentration, white emitting phosphors could be prepared. The present paper describes briefly an arsenic-activated zinc sulfide phosphor having properties similar to those of the phosphorus-activated zinc sulfide phosphor.

EXPERIMENTAL

Preparation

The materials used in the preparation of these phosphors were as follows:

(*a*) Zinc sulfide purified by the alkali process (2).

(*b*) "Ultra pure" sodium chloride obtained from the Mallinckrodt Chemical Company. This material was used as a flux.

(*c*) An arsenic compound, which in most of our preparations was arsenic trisulfide. This was prepared by precipitation from an acid solution of primary standard arsenic trioxide. Other arsenic compounds such as arsenic trioxide and zinc arsenate gave results similar to those obtained using arsenic trisulfide.

(*d*) The gases used in firing the phosphors were either commercial prepurified nitrogen, or hydrogen purified by means of a Deoxo unit and dried over barium oxide and phosphorus pentoxide.

The zinc sulfide, together with five per cent by weight of sodium chloride and an appropriate quantity of arsenic trisulfide, was fired in quartz test tubes which in turn were placed within larger quartz tubes through which either nitrogen or hydrogen was passed. The firing temperatures were usually in the neighborhood of 900°C. During the firing considerable quantities of arsenic were lost so that in every case the amount of arsenic remaining in the finished phosphor was much smaller than the quantity added to the unfired mix. The product from the first firing was not always completely homogeneous in its luminescent properties. By regrinding the phosphor, and then refiring it for a short period of time, a fairly homogeneous product resulted. Microscopic examination of the phosphor under excitation with 3650 Å ultraviolet light indicated that the greater part of the grains had the same fluorescence color, although there were some having a redder fluorescence and a still smaller number having a blue fluorescence. The finished phosphor was finally washed free of the flux with hot distilled water.

The properties of this phosphor are described below as a function of the concentration of arsenic, the firing atmosphere, and the firing temperature.

Luminescent Properties

Effect of the atmosphere during firing.—A series of preparations containing varying amounts of arsenic were fired at 900°C in pure nitrogen and hydrogen atmospheres for one-half hour. The emission spectra under excitation by 3650 Å ultraviolet light[2] of two typical products are shown in Fig. 1 and 2. The amounts of arsenic are given as the quantity added to the mixture before firing.

Heating in a reducing atmosphere yields a phosphor which has, in general, three emission bands. The one peaking at 4650 Å is the same band which appears when pure zinc sulfide is heated together with sodium chloride as a flux either in a reducing atmosphere or a neutral atmosphere and has been

[1] Manuscript received April 6, 1951. This paper prepared for delivery before the Washington Meeting, April 8 to 12, 1951.

[2] General Electric BH-4 high pressure mercury lamp with a red-purple filter.

attributed to activation by an excess of zinc at interstitial lattice sites. In addition, there is a band peaking at 6200 Å and another at 5200 Å, the latter appearing at the higher arsenic concentrations. The presence of the 5200 Å band is not clearly evident in the emission spectra of phosphors to which less than two per cent arsenic was added, if the emission spectra are taken at room temperature. When the temperature is raised to 100°C or higher, the blue

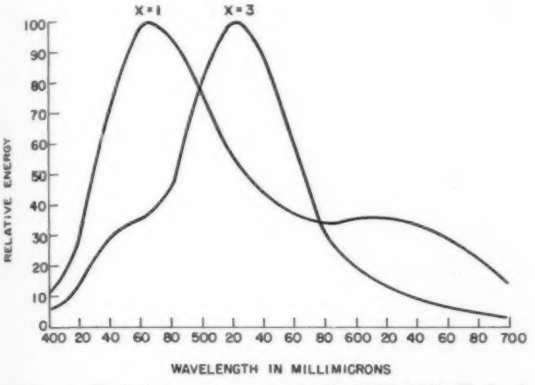

FIG. 1. Emission spectra of 100 ZnS:XAs:5NaCl fired in hydrogen at 900°C. Excitation—3650 Å. X is the amount by weight of arsenic present in the unfired phosphor mix.

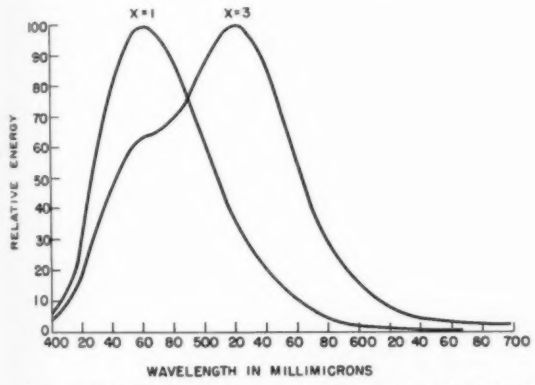

FIG. 2. Emission spectra of 100 ZnS:XAs:5NaCl fired in nitrogen at 900°C. Excitation—3650 Å. X is the amount by weight of arsenic present in the unfired phosphor mix.

emission band is quenched whereas the intensities of the green and orange bands are increased to some extent. In Fig. 3 are plotted the emission spectra at elevated temperatures of two phosphors to which one per cent of arsenic was added, one phosphor having been fired in nitrogen and the other in hydrogen. The blue bands of the two phosphors have been set equal to 100. The presence of the green band is evident in samples fired either in a reducing or a neutral atmosphere.

In contrast to the blue and green bands, the orange band does not appear unless a reducing atmosphere is used during the firing of the phosphor. This is evident from the various spectra.

Effect of arsenic concentration.—In order to determine the effect of arsenic concentration upon the relative intensity of the various emission bands, a series of samples were prepared to which varying amounts of arsenic were added as arsenic trisulfide. These were all fired for one-half hour at 900°C in a hydrogen atmosphere, reground, and refired for another fifteen minutes. Considerable amounts of

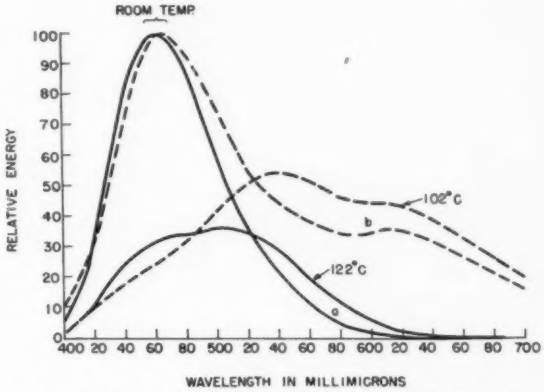

FIG. 3. Emission spectra of 100 ZnS:1As:5NaCl fired at 900°C, as dependent upon temperature during excitation with 3650 Å ultraviolet. One part of arsenic to 100 parts of ZnS was the composition of the unfired phosphor mix. *a*—Fired in nitrogen, *b*—fired in hydrogen.

TABLE I*

X	Color of fluorescence	
	3650 Å excitation	Cathode rays (5 kv)
0.01	warm white	light blue
0.1	light orange	cold white
0.5	warm white	cold white
1.0	cold white	cold white
2.0	greenish white	light green

* 100 ZnS:XAs:5NaCl; 900°C, hydrogen, ½ hour. X is the amount by weight of arsenic present in the unfired phosphor mix.

arsenic were lost during the firing process, as was evidenced by the appearance of elemental arsenic deposits on the cool portions of the firing tube. Attempts to determine analytically the amounts of arsenic in the finished phosphor have not been entirely successful to date; indications are that the amounts of arsenic remaining in the phosphor after firing are very much smaller than the amounts added, but vary in the same direction. Apparently very small quantities of arsenic can cause the appearance of the orange peak, and small changes in the arsenic content cause marked variations in the relative intensity of the various bands. This makes the problem

of reproducibility a difficult one unless the conditions of preparation are carefully controlled.

Table I lists the colors of the emitted light under 3650 Å excitation and cathode ray excitation (5 kv, defocused spot of about 5 μa/cm^2). The emission spectra for this series under 3650 Å excitation are

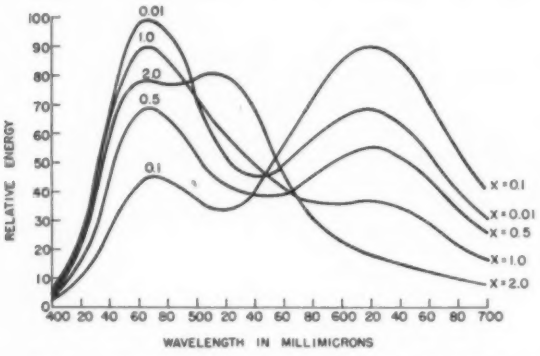

FIG. 4. Emission spectra of 100 ZnS:XAs:5NaCl fired in hydrogen at 900°C, for different amounts of arsenic added to the unfired phosphor mix. Excitation—3650 Å.

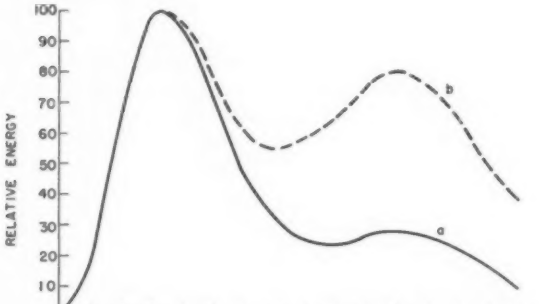

FIG. 5. Emission spectra of 100 ZnS:0.5As:5NaCl fired in hydrogen at 900°C. 0.5 parts of As to 100 parts of ZnS was the composition of the unfired phosphor mix. *a*—3650 Å excitation, *b*—cathode ray excitation (5 kv defocused spot, 5 μa/cm^2).

shown in Fig. 4. Here again the marked appearance of the green 5200 Å band at the highest arsenic concentrations should be noted.

The emission under cathode ray excitation is different than it is under long wavelength ultraviolet, in that the orange band is excited less efficiently relative to the blue band by cathode rays. This can be seen in Fig. 5 where the emission spectrum of a particular phosphor is shown for cathode ray and ultraviolet excitation. In both cases the intensity of the blue band has been adjusted to 100. The peak intensity of the orange band is some 65 per cent less under cathode rays than it is under ultraviolet excitation. The net result of this is that the color of the emitted light is always bluer under cathode rays than it is under 3650 Å ultraviolet excitation.

Effect of firing temperature.—Results on a series of preparations fired at different temperatures indicated that efficient materials are prepared by firing from about 800° to 900°C. Below 800°C the efficiency is poor and at 1000°C the products also showed low efficiency. White-emitting phosphors can be prepared by firing at 800° to 900°C but higher temperatures appear to give predominantly orange-emitting products. Above the transition point of zinc sulfide both the blue and orange bands shift toward shorter wavelengths.

Discussion

X-ray examinations of the arsenic-activated zinc sulfide phosphors failed to show any change in the lattice constant from that of unactivated zinc sulfide. This was true even for a sample to which a large amount (about 10%) of arsenic was added as arsenic trisulfide and the mixture fired in a sealed quartz tube to prevent loss of arsenic. The probable reason for the failure to find any significant change in the lattice constant is the very small quantities of arsenic that are present in the finished phosphor.

Because of these small concentrations, attempts to determine the oxidation state of the arsenic by chemical means were quite impossible. As in the case of other activated zinc sulfide phosphors, therefore, it would be fruitless to speculate on either the oxidation state of the activator or its position in the lattice without more definite information relating to these problems.

Acknowledgment

The emission spectra were determined by Miss Gwen Lloyd and Dr. F. J. Studer of our group. A great deal of work on the analysis for arsenic was done by Dr. E. W. Balis and Mr. L. B. Bronk of this laboratory.

Any discussion of this paper will appear in a Discussion Section, to be published in the June 1952 issue of the JOURNAL.

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Copper-Activated Aluminosilicate Phosphors[1]

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ABSTRACT

A new system of blue-luminescing, copper-activated aluminosilicate phosphors, corresponding to the general formula $x(yM^{I}_{2}O, zM^{II}O)\cdot pAl_2O_3\cdot qSiO_2$, is reported. These phosphors can be synthesized from any combination of Group IA and Group II metals, and they can tolerate a wide variation in the quantities of all the oxide components, including the copper activator.

Excitation and emission spectra are included for several typical phosphors, showing the relatively slight effects of variation in composition. The major excitation peak is in the neighborhood of 2600 Å. The emission spectra resemble that of $CaWO_4$, although the luminescence is slightly "whiter" and only one third as bright. The luminescence efficiency of these phosphors is nearly independent of temperature up to 150°C, and at 115°C their brightness is equal to that of $CaWO_4$.

INTRODUCTION

During earlier studies on activated zeolite minerals (1), hydrous aluminum silicates of alkali and alkaline earth metals, it was observed that luminescence developed after dehydration by heating at high temperatures. There followed an attempt to synthesize such zeolites by direct fusion of the oxide components. The luminescent products which were obtained were not zeolites, however, and further investigation of these products led to the development of the phosphor system described in this paper.

The luminescent materials included in this new phosphor system are copper-activated, alkali-plus-divalent-metal mixed aluminosilicates of the general formula $x(yM_2^{I}O, zM^{II}O)\cdot pAl_2O_3\cdot qSiO_2$, where the quantities x, y, z, p, and q may vary over wide ranges as discussed below. M^{I} may be Na, K, or Li; M^{II} may be Be, Ca, Mg, Sr, Ba, Zn, or Cd. Luminescence activation is effected by the incorporation of small amounts of copper.

Little is known as yet of the crystal structure of these aluminosilicates. Their x-ray diffraction powder patterns are complex and indicate crystalline compounds of a low order of symmetry. Many of the phosphors are undoubtedly mixtures of various aluminosilicates.

The phosphors respond to cathode-ray excitation as well as to ultraviolet radiation, with a blue luminescence resembling that of calcium tungstate, but with approximately one third the photoluminescence efficiency of the latter. Neither the luminescence intensity nor the color of the phosphor is critically dependent on chemical composition or conditions of preparation. The brightness of the phosphors is only slightly dependent on temperature between −150° and +150°C, and is not completely quenched even at 500°C.

[1] Manuscript received March 9, 1951. This paper prepared for delivery before the Washington Meeting, April 8 to 12, 1951.

PREPARATION

The reagents used in the preparation of the phosphors, with the exception of the silica, were C.P. grade chemicals, without further purification. The silica was in the form of high purity, finely divided silicic acid (Mallinckrodt's "special bulky"). The reagents were mixed by ballmilling with C.P. grade acetone in porcelain jars for 2 hr. The charge was then filtered, oven-dried at about 100°C, fired in uncovered fused silica crucibles in an electric furnace at 1150°C for 2 hr, and finally allowed to cool to room temperature. Other firing temperatures were tried in preliminary test runs, but 1150°C was chosen as effecting complete reaction with a minimum of sintering. The fired product was generally quite coarse, the degree of sintering increasing with increasing alkali content.

Chemical Composition

Nearly 300 samples of varying composition and brightness have been synthesized. One of the brightest phosphors was prepared from the following composition: Na_2O, 0.5 mole; CaO, 0.5 mole; Al_2O_3, 1 mole; SiO_2, 6 moles; CuO, 0.02 mole. Table I lists some of the variations in composition which have been investigated, expressed as the number of moles of the oxide components. Any pair of mole quantities of Al_2O_3:SiO_2 (p:q values) within a bracketed group can be combined with any pair of y:z mole quantities of $M_2^{I}O$:$M^{II}O$ in the corresponding group.

The brightness of the phosphors varies with the composition. The brighter preparations are those with higher concentrations of SiO_2. In the group of

phosphors where $x = 1$ ($Na_2O + CaO$) the luminescence intensity increases with increasing concentration of SiO_2, and reaches a maximum at a p:q value of 1:6, then tapers off gradually. The total mole concentration of ($M_2^IO + M^{II}O$), the x-values in Table I, may also be varied, phosphors having been synthesized from compositions in which $x = 0.5$, 1, or 2. A value of $x = 0.5$ or 1 seems the most desirable. Compositions with $x = 0.5$ ($Na_2O + CaO$) yield nonsintered products which need no pulverizing; those with $x = 1$ ($Na_2O + CaO$) form slightly brighter phosphors. The mole quantities, y and z, may be varied as indicated in Table I, but the brightest blue phosphors are those in which y equals z, or is slightly greater.

TABLE I. *Variations in composition of the type formula* $x(yM_2^IO, zM^{II}O)\cdot pAl_2O_3\cdot qSiO_2$, *expressed as number of moles of oxide components. Other variations are feasible*

x	(y:z)	:	p:q
0.5	0 :0.5 0.25:0.25 0.5 :0	:	3*:2 1 :1 3 :9 1 :3 1 :4 1 :5 1 :6 1 :7 1 :9
1	0 :1 0.3:0.7 0.5:0.5 0.7:0.3 1 :0	:	3 :2 1 :3 3 :9 1 :4 1 :5 1 :6 1 :7 1 :9
2	0 :2 0.4:1.6 1 :1 1.6:0.4 2 :0	:	3 :9 1 :6 1 :9

* The 3:2 compositions yield very dim phosphors. Compositions with higher p-values are nonluminescent.

Phosphors can be prepared in which M^I is any metal, or mixture of metals, of Group 1A, and M^{II} is any metal, or mixture of metals, of Group II. Phosphors containing Ba, Zn, Cd, or Li are considerably less bright than the Ca or Na analogs. Approximately one half the Ca may be replaced by Ba or Cd, and one half the Na by Li without appreciable loss in luminescence intensity. Ba (or Sr)-plus-Na phosphors, in which $x = 1$, emit more in the green and yellow regions than the other analogs.

The concentration of the activator should represent about 0.003 mole CuO for each mole of silica present in the phosphor, but may be varied approximately within the range of 0.0005–0.01 mole and still produce moderately bright phosphors. In preparations containing p:q values of 1:9, for example, the luminescence is of moderate intensity at a total CuO concentration of 0.003 mole, becoming brighter with increasing CuO and reaching a maximum brightness at 0.03 mole total CuO, then decreasing until at 0.1 mole total CuO the phosphor is dim.

Excitation Spectra

Excitation spectra of the phosphors were obtained by means of a Beckman hydrogen lamp and Model DU quartz spectrophotometer in combination with a 1-P28 photomultiplier tube, d-c amplifier, and Esterline-Angus recorder. Various Corning filters were used between the sample and photomultiplier to eliminate reflected ultraviolet light and to determine whether the spectral distribution was a function of the exciting wavelength. The excitation spectra were recorded through each of the following Corning filter combinations: No. 9700 + 5840, No. 9700 + 9780, and No. 9700 + 3060, so that any phosphor emission in the near ultraviolet as well as the blue and yellow regions of the spectrum could be examined. Peak excitation was observed in the neighborhood of 2600 Å. There was no difference in the shape of the excitation spectrum as the filters were changed, indicating that the emission spectrum was independent of any change in frequency of the exciting light.

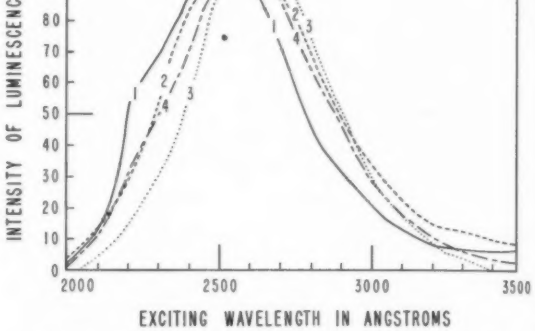

Fig. 1. Excitation spectra of phosphors with varied $Na_2O + CaO$ content. All peaks set equal to 100.
1 = $Na_2O\cdot Al_2O_3\cdot 6SiO_2$:Cu
2 = $CaO\cdot Al_2O_3\cdot 6SiO_2$:Cu
3 = $(0.5Na_2O, 0.5CaO)\cdot Al_2O_3\cdot 6SiO_2$:Cu
4 = $0.5Na_2O\cdot Al_2O_3\cdot 6SiO_2$:Cu

The excitation spectra illustrated in Fig. 1 are qualitative only, being uncorrected for spectral response of the phototube and for the intensity of the exciting light. In addition to the 2600 Å excitation peak, those phosphors having one or more moles total $Na_2O + CaO$ show a secondary peak at about

2200 Å. The latter peak may not be real since the energy output of the lamp-monochromator system used drops rapidly below 2300 Å, and what appears as a peak at 2200 Å may be the edge of an absorption band actually peaking at much shorter wavelengths.

Fig. 1 illustrates the effect on the excitation spectrum of varied Na_2O + CaO content in phosphors of otherwise identical composition. The 2200 Å excitation "peak" is pronounced in phosphors with high Na_2O content; it is missing in phosphors containing only one-half mole total Na_2O (where $y:z$ = 0.5:0). The one-mole Na_2O composition (where $y:z$ = 1:0) also shows a shift of the major excitation peak to shorter wavelengths. The excitation spectra of phosphors with varied Al_2O_3 + SiO_2 content are quite similar. Peak excitation occurs at 2500 Å or 2600 Å. Other chemical constituents being equal, the effect of increased SiO_2 is a tendency to suppress the 2200 Å "peak." The effect of increasing the CuO concentration in the phosphors is also a suppression of the 2200 Å "peak."

Emission Spectra

Emission spectra, under 2537 Å excitation, were determined with an automatically recording spectroradiometer (2). The luminescence emission ranges from the blue through the yellow regions of the spectrum. Fig. 2 shows emission spectra of a series of phosphors with varied Na_2O + CaO content. Phosphors containing CaO but no Na_2O are dim and emit chiefly in the blue. Introduction of Na_2O into the phosphor shifts the emission toward the yellow; from a 4500 Å peak to a 5050 Å peak for the compositions with x = 1 (Na_2O + CaO); from a 4350 Å peak to a 4650 Å peak for those with x = 0.5 (Na_2O + CaO). Intermediate Na_2O + CaO compositions have the blue tungstate-like, and the brightest, emission.

The emission of one of the brightest phosphors prepared to date may be compared with that of calcium tungstate in curves included in Fig. 3. The emission of the aluminosilicates is slightly "whiter" than, but only one third as bright as, that of calcium tungstate.

The quantities of Al_2O_3 + SiO_2 in the phosphors have comparatively little effect on the spectral distribution of the emission (see Fig. 3). There is a slight progressive shift toward the blue end of the spectrum as the $p:q$ values are changed from 1:3 (4850 Å peak) to 1:4 (4750 Å), 1:5 (4650 Å), and 1:6 (4650 Å). The luminescence emission of the 1:6, 1:7, and 1:9 compositions shows nearly identical spectral distribution. The 3:9 composition exhibits a further shift into the blue and a broadening of the emission peak (4350–4550 Å).

As mentioned earlier, the range in concentration of copper activator tolerated by the phosphors is considerable. There is close similarity in spectral emission, both as to distribution and intensity, of phosphors containing 0.01, 0.03, and 0.08 mole of copper. In an attempt to whiten the emission of the

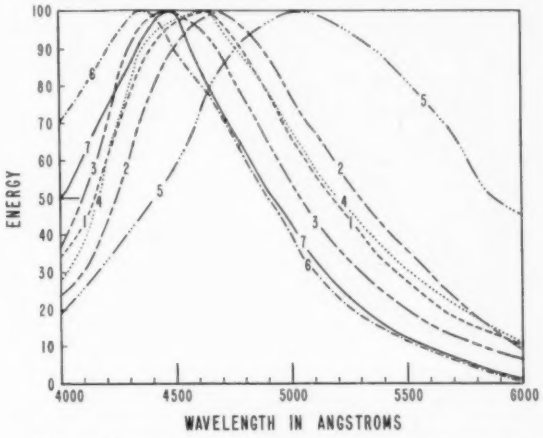

Fig. 2. Spectral emission curves showing the effect of varying the Na_2O and CaO content. Peaks of all curves set equal to 100. Actual relative peak heights: 1 = 100, 2 = 95, 3 = 94, 4 = 84, 5 = 37, 6 = 22, 7 = 11.

1 = $(0.5Na_2O, 0.5CaO)\cdot Al_2O_3\cdot 6SiO_2$:Cu
2 = $(0.7Na_2O, 0.3CaO)\cdot Al_2O_3\cdot 6SiO_2$:Cu
3 = 0.5 $(0.25Na_2O, 0.25CaO)\cdot Al_2O_3\cdot 6SiO_2$:Cu
4 = $0.5Na_2O\cdot Al_2O_3\cdot 6SiO_2$:Cu
5 = $Na_2O\cdot Al_2O_3\cdot 6SiO_2$:Cu
6 = $0.5CaO\cdot Al_2O_3\cdot 6SiO_2$:Cu
7 = $CaO\cdot Al_2O_3\cdot 6SiO_2$:Cu

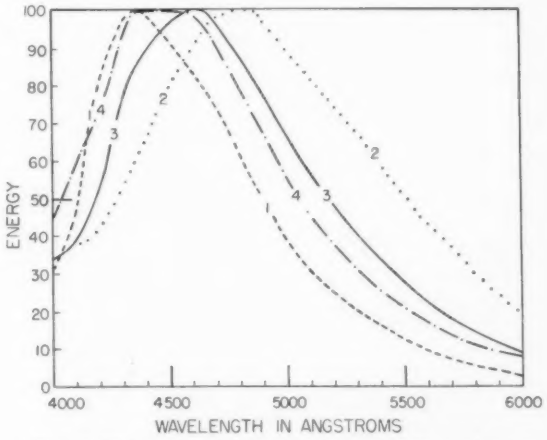

Fig. 3. The effect of varied Al_2O_3 and SiO_2 content on spectral emission. The $CaWO_4$ curve is included for comparison with that of a typical bright aluminosilicate (curve 3). Peaks of all curves set equal to 100. Actual relative peak heights: 1 = 100, 2 = 15, 3 = 37, 4 = 28.

1 = Sylvania $CaWO_4$
2 = $(0.5Na_2O, 0.5CaO)\cdot Al_2O_3\cdot 3SiO_2$:Cu
3 = $(0.5Na_2O, 0.5CaO)\cdot Al_2O_3\cdot 6SiO_2$:Cu
4 = $(0.5Na_2O, 0.5CaO)\cdot Al_2O_3\cdot 9SiO_2$:Cu

phosphors by sensitized luminescence, manganese or samarium was introduced into selected Cu-bearing phosphors, but with little success. Phosphors activated by titanium[2] are even less efficient, showing only about one tenth the peak emission intensity and different spectral distribution.

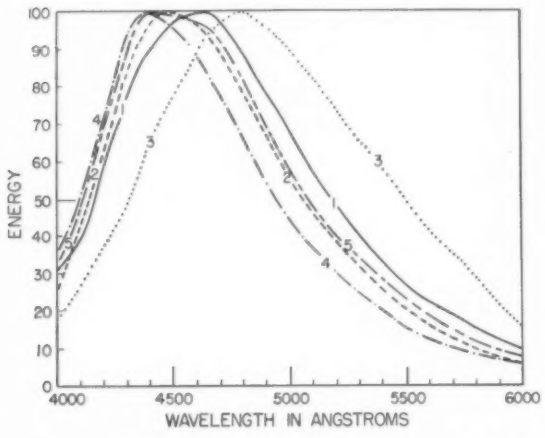

FIG. 4. Luminescence emission of phosphors with "substitute" metals, compared with the Na-Ca compositions. Peaks of all curves set equal to 100. Actual relative peak heights: 1 = 100, 2 = 96, 3 = 58, 4 = 94, 5 = 76.

1 = $(0.5Na_2O, 0.5CaO)\cdot Al_2O_3\cdot 6SiO_2$:Cu
2 = $(0.5Na_2O, 0.5MgO)\cdot Al_2O_3\cdot 6SiO_2$:Cu
3 = $(0.5Na_2O, 0.5SrO)\cdot Al_2O_3\cdot 6SiO_2$:Cu
4 = $0.5(0.25Na_2O, 0.25CaO)\cdot Al_2O_3\cdot 6SiO_2$:Cu
5 = $0.5(0.25Na_2O, 0.25SrO)\cdot Al_2O_3\cdot 6SiO_2$:Cu

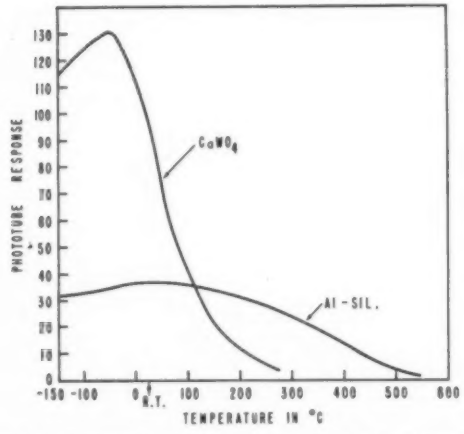

FIG. 5. Temperature dependence of the luminescence efficiency of a typical bright aluminosilicate, under 2537 Å excitation, compared with $CaWO_4$. Phototube response measured at peak emission (4650 Å—aluminosilicate; 4350 Å—$CaWO_4$). Aluminosilicate = $(0.5Na_2O, 0.5CaO)\cdot Al_2O_3\cdot 6SiO_2$:Cu.

[2] The possibility of Ti as an intensifier-activator was suggested by H. W. Leverenz.

The emission spectra of some phosphors containing metals other than Ca and Na are illustrated in Fig. 4. The emission peak varies with the identity of the metal or combination of metals as well as with the total mole concentration (x-values) of alkali plus divalent metal. Where $x = 0.5$ there is considerably less variation in the emission (4350–4450 Å peaks) of phosphors containing metals such as Mg, Be, or Sr than where $x = 1$ (peaks vary from 4450–4900 Å). Compositions with $x = 0.5$ also show a narrowing of the emission band.

The spectral distribution of the aluminosilicates' emission undergoes negligible change with change in temperature. The equipment used for the low temperature studies (−50°C with dry ice; −150°C with liquid nitrogen) was described in an earlier paper (2). The curves in Fig. 5 illustrate the temperature-dependence of the luminescence efficiency of a bright aluminosilicate phosphor, $(0.5Na_2O, 0.5CaO)\cdot Al_2O_3\cdot 6SiO_2$:Cu, as compared with $CaWO_4$. Measurements were made at the peak of the spectral distribution curves, at 4650 Å for the aluminosilicate and 4350 Å for $CaWO_4$. The aluminosilicate maintains its efficiency almost unchanged up to 150°C. At about 115°C the aluminosilicate is comparable in brightness to $CaWO_4$, which has undergone a two-thirds loss in efficiency. The aluminosilicate maintains at least 50 percent of its room-temperature efficiency up to 350°C.

The host crystals—unactivated soda-lime aluminosilicates—may exhibit barely detectable visible emission of the order of 0.01 that of the comparable phosphors. Similarly feeble luminescence, or none whatsoever, is seen in the aluminosilicate lattice containing neither alkali nor divalent metal when activated by copper.

Several Cu-activated silicates have been reported in the literature and cited by Kroeger (3) and Leverenz (4). These are simple ortho- or metasilicate compositions, or silicate glasses. Judging from the x-ray diffraction patterns, the aluminosilicate:Cu phosphors described in this paper do not seem to resemble either ortho- or metasilicates. Cu-activated ortho- and metasilicate compositions have also been prepared, but these luminesce dimly at best, and some are inert glassy products. Cu-activated silica, prepared by the same technique, also emits feebly in the visible spectrum.

Cu-activated α-Al_2O_3 and $CaAl_2O_4$:Cu are cited by Kroeger (3) as luminescing green or blue, and several Mn- or Cr-activated aluminates are described by Leverenz (4). Cu-activated Al_2O_3 and $CaAl_2O_4$:Cu, prepared by the same technique as the aluminosilicate phosphors, do not luminesce visibly, but $NaAlO_2$:Cu does show weak blue luminescence. The

authors have also synthesized Cu-activated aluminosilicates rich in Al (Al:Si values of 1:1, 3:2, 5:1, 10:1). Of these, the 5:1 and 10:1 compositions are inert; the 1:1 and 3:2 emit feebly in the visible. These products all give x-ray diffraction patterns suggestive of α-Al_2O_3. The typical bright phosphors of the aluminosilicate system, however, are far from the extreme end-compositions mentioned above, and exhibit 100-fold increase in luminescence output under ultraviolet excitation.

Any discussion of this paper will appear in a Discussion Section, to be published in the June 1952 issue of the JOURNAL.

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Luminescent Barium and Magnesium Halophosphates[1]

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ABSTRACT

Uranium is the principal useful activator in magnesium and barium halophosphates, giving rise to efficient and fairly saturated yellow-green luminescence. Barium chlorophosphate:U, in particular, shows a strong emission peaking at 5300 Å under both short and long ultraviolet excitation. Details of absorption characteristics and variations in base composition are discussed briefly.

Magnesium Halo (Fluoro) Phosphate

The magnesium compound was discovered before the one with barium, and a brief account of it is given first. Raw material magnesium ammonium phosphate was prepared by precipitation from magnesium chloride (AnalaR) solution with a solution of diammonium hydrogen phosphate (AnalaR) in the presence of ammonia. Magnesium fluoride was prepared similarly from solutions of magnesium chloride and potassium fluoride. The fluoride:phosphate ratio used was approximately 1:3 moles, enough magnesium oxide (AnalaR) being added in certain cases to produce the fluoro-orthophosphate during the firing process.

A large number of activators were tried at firing temperatures between 900° and 1100°C. Only silver, thallium, and uranium were found to give luminescent materials, and these only with the fluoro-compound. They were all of relatively low efficiency, silver giving a violet luminescent color, thallium blue-violet, and uranium a green color, under short ultraviolet (u.v.) irradiation. The uranium-activated material was excited by both long and short u.v. radiation and by cathode rays.

The optimum amount of added uranium was 2 to 2.5 per cent of UO_3 (reagent grade), calculated by weight of the magnesium ammonium phosphate. The best firing conditions were at 1050°C for 20 min, for very small quantities in a covered silica crucible. Too high a temperature or too long a firing time led to the development of a nonfluorescent outer sheath around the crucible charge. Omission of the magnesium fluoride or its replacement by the equivalent amount of magnesium chloride in the uranium-activated mixture gave nonluminescent materials. No improvement was obtained by alterations in the amount of fluoride used in the mixture. Variations in the basicity of the magnesium phosphate, produced by additions of magnesium oxide or ammonium phosphate to the mixture, reduced the fluorescence.

[1] Manuscript received February 23, 1951. This paper prepared for delivery before the Washington Meeting, April 8 to 12, 1951.

Barium Halophosphate

Preparation of Raw Materials

Solutions were made of 1.00 kg of barium chloride ($BaCl_2 \cdot 2H_2O$, AnalaR) in 3 l of distilled water, and of 0.40 kg diammonium phosphate (AnalaR) in 2 l of water. Both solutions were filtered through finest available filter papers and heated to boiling. The phosphate solution was added to the barium chloride at a controlled rate, e.g., through a 0.04 in. diam jet, with constant agitation. A 1:1 mixture of water and ammonia of sp gr 0.880 was then added until the solution was just alkaline to litmus. After two successive washes, followed by decantation, with 4 l each of boiling water, the solid was filtered off and dried at 105°C. The yield was approximately 800 g, i.e., about 97 per cent of theoretical calculated as $Ba_3(PO_4)_2$. The material, however, is not pure triorthophosphate; it is very slightly acid and can be corrected to give $Ba_3(PO_4)_2$ after firing by small prefiring additions of barium carbonate.

Of various possible and tried methods of preparing BaF_2, the following is preferred. Solutions were made of 500 g $Ba(NO_3)_2$ (AnalaR) in 1.5 l of distilled water, and of 150 g of ammonium fluoride in 1.2 l of water. The latter material was xNH_4F $(1-x)$ NH_4HF_2 (AnalaR), where x is close to, but less than, unity. The nitrate solution was boiled to dissolve all the solid, filtered, and kept hot to avoid recrystallization. The fluoride solution was warmed, filtered, brought to a boil, and added to the barium nitrate at a controlled rate with stirring, as in the case of the phosphate above. After allowing the precipitate to settle for at least 15 hr, the top liquor was removed and the precipitate washed twice with 3 l at a time of boiling water. The solid was filtered off, washed finally with 1 l of hot water on the filter, and dried at 110°C. The yield was about 300 g, equivalent to about 92 per cent of theoretical.

Preparation of Phosphors and Variations in Composition

Mixtures of barium phosphate, barium chloride or fluoride, barium carbonate, and uranium trioxide have been made in the dry and wet way, by hand mixing and by ballmilling. When uranyl nitrate was used instead of UO_3, the mixtures were all wet, the nitrate being used as a solution. A slight preference is felt for this method as it seems to give more uniform mixes.

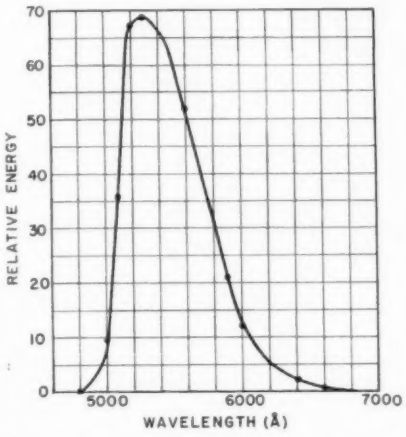

FIG. 1. Emission of barium chlorophosphate:U, banded structure not shown, excited by 2537 Å radiation.

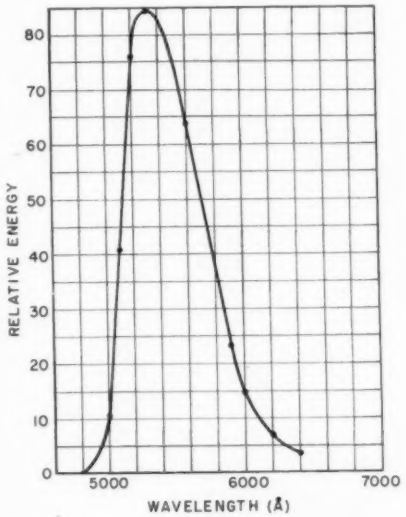

FIG. 2. Emission of barium chlorophosphate:U, banded structure not shown, excited by 3650 Å radiation.

Firing can be carried out in silica or porcelain crucibles, both of which take on a lining of adherent barium halophosphate, which it seems best to leave in place. The firing had to be conducted in a number of stages to prevent the material from becoming excessively hard and sintered. As firing progressed the tendency to sinter became less and the temperature could be gradually raised. First firings were usually made between 850° and 900°C for 30 to 40 min. Later firings could be made as high as 1000°C for 1 hr or at 900°C for 5 hr. Firing at 1100°C caused a decided drop in luminescent output.

As an example, a typical mixture was composed of: 160 g barium phosphate (ppt.), 5.2 g $BaCO_3$, 22.4 g $BaCl_2 \cdot 2H_2O$, and 21.1 g $UO_2(NO_3)_2$ in solution. These ingredients were ballmilled as a paste in water until thoroughly mixed (4–24 hr), and after separation of the balls, dried at 105°–150°C. The firings, with intermediate grindings, were:

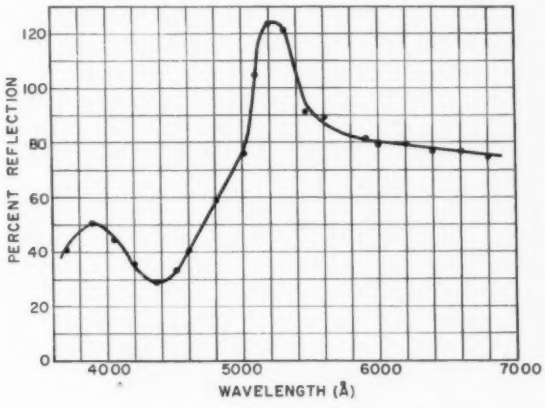

FIG. 3. Reflection of barium chlorophosphate:U

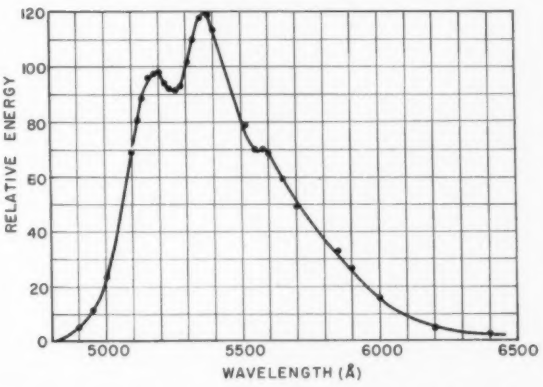

FIG. 4. Spectral distribution of barium chlorophosphate: U emission in 80-w fluorescent lamp, showing banded structure.

1. 870°C	30 min	4. 930°C	40 min
2. 870	30	5. 930	60
3. 930	30	6. 930	120

Further firings may be given, but little improvement in brightness of fluorescence is achieved. After comminution and sieving the material could be

washed in boiling water if desired. No apparent harm or improvement was noted.

The first phosphors were prepared with an equivalent amount of BaF_2 instead of the chloride. This gave results similar to later ones using the chloride, but in general the luminescence takes a longer firing to develop, and the ultimate brightness is somewhat less.

Silver activator gave poor violet, and easily light-blackened (photosensitive) blue-violet luminescing phosphors with the fluoro- and chlorophosphate, respectively. Thallium gave nonluminescent and poor whitish luminescent materials, respectively. Uranium gave a good green fluorescence in both cases, and also a moderately good one without any positive halide addition, but this may have been due to a little residual chloride absorbed by the phosphate precipitate.

It is interesting to note that in general the fluoro-compound gives better results with the magnesium phosphate phosphor, and the chloro-compound with the barium one, particularly with the uranium-activated materials. A mixed 1:1 fluoro-chloro barium phosphate with uranium was ultimately nearly as efficient as the chloro-compound, but the luminescence was very slow in developing. Changes in basicity of the phosphate by addition of barium carbonate or ammonium phosphate showed that best results were obtained when the phosphate approximated $Ba_3(PO_4)_2$. This was achieved by the addition of 3 to 3.5 per cent of $BaCO_3$, by weight of the dry phosphate precipitate. A 30 per cent addition of $BaCO_3$ caused a brown discoloration in the final product which was nonluminescent, and a 7 per cent addition gave results very similar to those obtained with no addition.

Barium Halophosphate:Uranium Phosphor

Variation in the amount of uranium oxide (or the equivalent amount of uranyl nitrate) was tried over a range from 1.25 to 7.5 per cent by weight of the barium phosphate. With the lowest amount, unactivated portions (showing as white patches when viewed in daylight, as against the greenish yellow color of the phosphor powder) appeared in the fired crucible charges. This lack of adequate diffusion was more pronounced with the oxide activator. In the range between 5 and 7.5 per cent UO_3, there was no appreciable difference in the luminescence obtained, and 7.5 per cent was usually used.

The phosphors are dense powders, similar in color to uranyl salts under ordinary light. The fluorescent color is a relatively saturated green when excited by long or short wavelength u.v. radiation. There is also a weak green response to cathode ray excitation. The brightness with long wavelength u.v. excitation is comparable with that of ZnS:Cu, but much more saturated in color; under short u.v. it compares with that of Zn_2SiO_4:Mn.

Fig. 1 and 2 show emission curves of phosphor powders excited, respectively, by an unfiltered, quartz jacketed, low pressure mercury lamp, and a filtered high pressure mercury vapor lamp (Mazda 125-w type MBW). It will be seen that the curves are very similar in shape and that both show a maximum at about 5300 Å. No special effort was made with these curves to show the more detailed band structure of the luminescent spectrum which is more clearly shown in Fig. 4.

No appreciable afterglow has been noticed with any of the exciting radiations. Fig. 3 shows the reflection characteristics for barium chlorophosphate:U in the visible and near u.v. regions. The relatively strong absorption at about 4350 Å is worthy of notice. We believe that this absorption could be used to reduce the color distortion effect of the strong 4358 Å mercury line in the low pressure mercury (fluorescent) lamps. The peak near 5200 Å is probably caused by luminescence.

The phosphor suffers a definite loss of luminescent efficiency when subjected to prolonged milling, and this has affected the performance in lamps coated in the usual manner with a suspension of the phosphor in nitrocellulose solution. By prolonged ball-milling the average grain size could be reduced from about 12–20 μ to about 3–4 μ, but there is a considerable loss in fluorescent output. This loss can be restored in part by refiring at 900°–950°C for about ½ hr. Best results to date give an initial lpw figure of 38 to 40 with an 80-w, 5-ft lamp. The maintenance is comparable to that of Zn_2SiO_4:Mn.

The emission curve of Fig. 4 shows some fine structure in the spectral variation of relative energy with wavelength. The phosphor was excited within an 80-w lamp.

Acknowledgment

We wish to express our thanks to Mr. M. G. Clarke of the B. T. H. Research Laboratories, for his help in the preparation of the curves shown in Fig. 1 to 4, and to Mr. L. J. Davies, Director of Research, for permission to publish this paper.

Any discussion of this paper will appear in a Discussion Section, to be published in the June 1952 issue of the JOURNAL.